

(19) World Intellectual Property Organization
International Bureau(43) International Publication Date
15 May 2003 (15.05.2003)

PCT

(10) International Publication Number
WO 03/039259 A1(51) International Patent Classification⁷: A01N 43/90

DOBLER, Markus [CH/CH]; Syngenta Crop Protection AG, Schwarzwaldallee 215, CH-4058 Basel (CH).

(21) International Application Number: PCT/GB02/04734

(22) International Filing Date: 21 October 2002 (21.10.2002)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
0126914.1 8 November 2001 (08.11.2001) GB

(71) Applicants (for all designated States except US): SYNGENTA LIMITED [GB/GB]; European Regional Centre, Priestley Road, Surrey Research Park, Guildford, Surrey GU2 7YH (GB). SYNGENTA PARTICIPATIONS AG [CH/CH]; Schwarzwaldallee 215, CH-4058 Basel (CH).

(72) Inventors; and

(75) Inventors/Applicants (for US only): WORTHINGTON, Paul, Anthony [GB/GB]; Syngenta Limited, Jealott's Hill International Research Centre, Bracknell, Berkshire RG42 6EY (GB). VALANCOGNE, Ingrid, Aurelie [FR/GB]; Syngenta Limited, Jealott's Hill International Research Centre, Bracknell, Berkshire RG42 6EY (GB). FAWKE, Delphine, Raymonde, Suzanne [FR/GB]; Syngenta Limited, Jealott's Hill International Research Centre, Bracknell, Berkshire RG42 6EY (GB).

(74) Agents: HOUGHTON, Malcolm, John et al.; Intellectual Property Department, Syngenta Limited, Jealott's Hill Research Centre, PO Box 3538, Bracknell RG42 6YA (GB).

(81) Designated States (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZM, ZW.

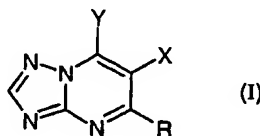
(84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— with international search report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: FUNGICIDES



(57) Abstract: The use as a plant fungicide of a compound of general formula (I); wherein R is H, halo, C₁-8? alkyl or cyano; X and Y are independently halo, C₁-8? alkoxy, C₁-8? alkylthio, aryloxy, arylthio, heteroaryloxy, heteroarylthio, aryl(C₁-4?)-alkoxy, heteroaryl(C₁-4?)alkoxy, aryl(C₁-4?)alkylthio, heteroaryl(C₁-4?)alkylthio, C₁-8? alkylamino, C₂-8? alkenylamino, C₂-8? alkynylamino, di(C₁-8?)alkylamino, di(C₂-8?)-alkenylamino, di(C₂-8?)alkynylamino, (C₂-8?)alkynylamino C₂-8? alkyl-(C₁-8?)alkylamino or C₂-8? alkenyl(C₁-8?)alkylamino arylamino, aryl(C₁-8? alkyl)amino, heteroarylamino, heteroaryl(C₁-8? alkyl) amino, aryl(C₁-4?)alkylamino, aryl(C₁-4?)alkyl-(C₁-8? alkyl)amino, heteroaryl(C₁-4?)alkylamino, heteroaryl(C₁-4?)alkyl (C₁-8? alkyl)amino, morpholino or piperidino, or Y is hydroxy, provided that when X is C₁-8? alkoxy, aryloxy, morpholino or piperidino, R and Y are not both halo; any of the foregoing alkyl, alkenyl, alkynyl, aryl, heteroaryl, morpholino or piperidino groups or moieties being optionally substituted. Also included are plant fungicidal compositions containing these compounds and many of the compounds themselves.



WO 03/039259 A1

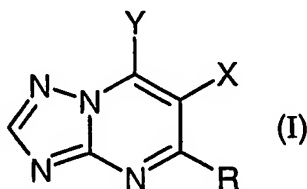
FUNGICIDES

This invention relates to the use as plant fungicides of certain substituted *s*-1,2,4-triazolo[1,5-*a*]pyrimidine compounds. It also relates to plant fungicidal compositions containing these compounds and to many of the compounds themselves.

5 There are many substituted *s*-1,2,4-triazolo[1,5-*a*]pyrimidines known from the patent literature as being useful for controlling phytopathogenic fungi. Examples of relevant patent publications include EP-A-0071792, EP-A-0550113, US 5593996, EP-A-0834513, WO 94/20501, WO 98/46607, WO 98/46608, WO 99/48893, EP-A-0945453, WO 99/41255, US 5985883, US 5986135, US 6242451 and US 6255309. Other substituted *s*-1,2,4-triazolo[1,5-*a*]pyrimidines are described in GB-A-1148629 and by Y. Makisumi in *Chem.*
10 *Pharm. Bull.* (Tokyo), 1961, 9, 801-808 & 808-814. These other triazolopyrimidines are reported as having a coronary vasodilative effect on animals (GB-A-1148629) or as being potential anticancer agents (Y. Makisuma).

The present invention is concerned with the provision of alternative substituted *s*-1,2,4-triazolo[1,5-*a*]pyrimidines for use as plant fungicides.
15

Thus, according to the present invention, there is provided the use as a plant fungicide of a compound of the general formula (I):



wherein R is H, halo, C₁₋₈ alkyl or cyano; X and Y are independently halo, C₁₋₈ alkoxy, C₁₋₈ alkylthio, aryloxy, arylthio, heteroaryloxy, heteroarylthio, aryl(C₁₋₄)alkoxy, heteroaryl(C₁₋₄)alkoxy, aryl(C₁₋₄)alkylthio, heteroaryl(C₁₋₄)alkylthio, C₁₋₈ alkylamino, C₂₋₈ alkenylamino, C₂₋₈ alkynylamino, di(C₁₋₈)alkylamino, di(C₂₋₈)alkenylamino, di(C₂₋₈)alkynylamino, C₂₋₈ alkenyl-(C₂₋₈)alkynylamino C₂₋₈ alkynyl(C₁₋₈)alkylamino or C₂₋₈ alkenyl(C₁₋₈)alkylamino arylamino, aryl(C₁₋₈ alkyl)amino, heteroarylamino, heteroaryl(C₁₋₈ alkyl)amino, aryl(C₁₋₄)alkylamino,
25 aryl(C₁₋₄)alkyl(C₁₋₈ alkyl)amino, heteroaryl(C₁₋₄)alkylamino, heteroaryl(C₁₋₄)alkyl (C₁₋₈ alkyl)amino, morpholino or piperidino, or Y is hydroxy, provided that when X is C₁₋₈ alkoxy, aryloxy, morpholino or piperidino, R and Y are not both halo; any of the foregoing alkyl, alkenyl, alkynyl, aryl, heteroaryl, morpholino or piperidino groups or moieties being optionally substituted.

In one aspect of the invention there is provided the use as a plant fungicide of a compound of the general formula (I) wherein R is H, halo, C₁₋₈ alkyl or cyano; X and Y are independently halo, C₁₋₈ alkoxy, C₁₋₈ alkylthio, aryloxy, arylthio, heteroaryloxy, heteroarylthio, aryl(C₁₋₄)alkoxy, heteroaryl(C₁₋₄)alkoxy, aryl(C₁₋₄)alkylthio, heteroaryl(C₁₋₄)alkylthio, C₁₋₈ alkylamino, C₂₋₈ alkenylamino, C₂₋₈ alkynylamino, di(C₁₋₈)alkylamino, arylamino, aryl(C₁₋₈ alkyl)amino, heteroarylamino, heteroaryl(C₁₋₈ alkyl)amino, aryl(C₁₋₄)alkylamino, aryl(C₁₋₄)alkyl(C₁₋₈ alkyl)amino, heteroaryl(C₁₋₄)alkylamino or heteroaryl(C₁₋₄)alkyl (C₁₋₈ alkyl)amino or Y is hydroxy, morpholino or piperidino, provided that when X is other than halo, R and Y are not both halo; any of the foregoing alkyl, alkenyl, alkynyl, aryl, heteroaryl, morpholino or piperidino groups or moieties being optionally substituted.

More specifically, there is provided the use as a plant fungicide of a compound of the general formula (I) wherein R is H, halo, C₁₋₈ alkyl or cyano; X is halo, C₁₋₈ alkylthio, arylthio, heteroaryloxy, heteroarylthio, aryl(C₁₋₄)alkylthio, heteroaryl(C₁₋₄)alkylthio, C₁₋₈ alkylamino, C₂₋₈ alkenylamino, C₂₋₈ alkynylamino, di(C₁₋₈)alkylamino, arylamino, aryl(C₁₋₈ alkyl)amino, heteroarylamino, heteroaryl(C₁₋₈ alkyl)amino, aryl(C₁₋₄)alkylamino, aryl(C₁₋₄)alkyl(C₁₋₈ alkyl)amino, heteroaryl(C₁₋₄)alkylamino or heteroaryl(C₁₋₄)alkyl (C₁₋₈ alkyl)amino; and Y is halo, hydroxy, C₁₋₈ alkoxy, C₁₋₈ alkylthio, aryloxy, arylthio, heteroaryloxy, heteroarylthio, aryl(C₁₋₄)alkoxy, heteroaryl(C₁₋₄)alkoxy, aryl(C₁₋₄)alkylthio, heteroaryl(C₁₋₄)alkylthio, C₁₋₈ alkylamino, C₂₋₈ alkenylamino, C₂₋₈ alkynylamino, di(C₁₋₈)alkylamino, arylamino, aryl(C₁₋₈ alkyl)amino, heteroarylamino, heteroaryl(C₁₋₈ alkyl)amino, aryl(C₁₋₄)alkylamino, aryl(C₁₋₄)alkyl(C₁₋₈ alkyl)amino, heteroaryl(C₁₋₄)alkylamino or heteroaryl(C₁₋₄)alkyl (C₁₋₈ alkyl)amino, morpholino or piperidino; any of the foregoing alkyl, alkenyl, alkynyl, aryl, heteroaryl, morpholino or piperidino groups or moieties being optionally substituted.

The compounds of the invention may contain one or more asymmetric carbon atoms and may exist as enantiomers (or as pairs of diastereoisomers) or as mixtures of such. However, these mixtures may be separated into individual isomers or isomer pairs, and this invention embraces such isomers and mixtures thereof in all proportions. It is to be expected that for any given compound, one isomer may be more fungicidally active than another.

Except where otherwise stated, alkyl groups and alkyl moieties of alkoxy, alkylamino, etc., suitably contain from 1 to 6, typically from 1 to 4, carbon atoms in the form of straight or branched chains. Examples are methyl, ethyl, *n*- and *iso*-propyl, *n*-, *sec*-, *iso*- and *tert*-

butyl, *n*-pentyl and *n*-hexyl. Examples of suitable optional substituents of alkyl groups and moieties include halo, hydroxy, C₁₋₄ alkoxy and C₁₋₄ alkoxy(C₁₋₄)alkoxy. Where the optional substituent is halo, the haloalkyl group or moiety is typically trichloromethyl or trifluoromethyl.

5 Alkenyl and alkynyl moieties also suitably contain from 1 to 6, typically from 1 to 4, carbon atoms in the form of straight or branched chains. Examples are allyl, 2-methylallyl and propargyl. Optional substituents include halo, typically fluoro, for example, 2,2,2-trifluoro-1-methylethyl.

Halo includes fluoro, chloro, bromo and iodo. Most commonly it is fluoro, chloro or
10 bromo.

Aryl is usually phenyl but also includes naphthyl, anthryl and phenanthryl.

Heteroaryl is typically a 5- or 6-membered aromatic ring containing one or more O, N or S heteroatoms, which may be fused to one or more other aromatic or heteroaromatic rings, such as a benzene ring. Examples are thienyl, furyl, pyrrolyl, isoxazolyl, oxazolyl,
15 oxadiazolyl, pyrazolyl, imidazolyl, triazolyl, isothiazolyl, tetrazolyl, thiadiazolyl, pyridyl, pyrimidinyl, pyrazinyl, pyridazinyl, triazinyl, benzofuryl, benzothienyl, dibenzofuryl, benzothiazolyl, benzoxazolyl, benzimidazolyl, indolyl, quinolinyl and quinoxalinyl groups and, where appropriate, N-oxides thereof.

Any of the aryl or heteroaryl values are optionally substituted by one or more,
20 typically 1, 2 or 3, substituents of the kind that are customarily present in pesticidal compounds. Substituents which may be present include one or more of the following: halo, hydroxy, mercapto, C₁₋₈ alkyl (especially methyl and ethyl), C₂₋₆ alkenyl (especially allyl), C₂₋₆ alkynyl (especially propargyl), C₁₋₆ alkoxy (especially methoxy), C₂₋₆ alkenyloxy (especially allyloxy), C₃₋₆ alkynyloxy (especially propargyloxy), halo(C₁₋₈)alkyl (especially
25 trifluoromethyl), halo(C₁₋₆)alkoxy (especially trifluoromethoxy), C₁₋₆ alkylthio (especially methylthio), hydroxy(C₁₋₆)alkyl, C₁₋₄ alkoxy(C₁₋₄)alkyl, C₁₋₄ alkoxy(C₁₋₄)alkoxy, C₃₋₆ cycloalkyl, C₃₋₆ cycloalkyl(C₁₋₄)alkyl, optionally substituted aryl (especially optionally substituted phenyl), optionally substituted heteroaryl (especially optionally substituted pyridyl or pyrimidinyl), optionally substituted aryloxy (especially optionally substituted
30 phenoxy), optionally substituted heteroaryloxy (especially optionally substituted pyridyloxy or pyrimidyloxy), optionally substituted arylthio (especially optionally substituted phenylthio), optionally substituted heteroarylthio (especially optionally substituted

pyridylthio or pyrimidinylthio), optionally substituted aryl(C₁₋₄)alkyl (especially optionally substituted benzyl, optionally substituted phenethyl and optionally substituted phenyl n-propyl), optionally substituted heteroaryl(C₁₋₄)alkyl (especially optionally substituted pyridyl- or pyrimidinyl(C₁₋₄)alkyl), optionally substituted aryl(C₂₋₄)alkenyl (especially optionally substituted phenylethenyl), optionally substituted heteroaryl(C₂₋₄)alkenyl (especially optionally substituted pyridylethenyl or pyrimidinylethenyl), optionally substituted aryl(C₁₋₄)alkoxy (especially optionally substituted benzyloxy and phenethyloxy), optionally substituted heteroaryl(C₁₋₄)alkoxy (especially optionally substituted pyridyl- or pyrimidinyl(C₁₋₄)alkoxy), optionally substituted aryloxy(C₁₋₄)alkyl (especially phenoxy-methyl), optionally substituted heteroaryloxy(C₁₋₄)alkyl (especially optionally substituted pyridyloxy or pyrimidinyl(C₁₋₄)alkyl), optionally substituted aryl(C₁₋₄)alkylthio (especially optionally substituted benzylthio and phenethylthio), optionally substituted heteroaryl(C₁₋₄)alkylthio (especially optionally substituted pyridyl or pyrimidinyl(C₁₋₄)-alkylthio), optionally substituted arylthio(C₁₋₄)alkyl (especially phenylthio-methyl), optionally substituted heteroarylthio(C₁₋₄)alkyl (especially optionally substituted pyridylthio- or pyrimidinylthio(C₁₋₄)alkyl), acyloxy, including C₁₋₄ alkanoyloxy (especially acetyloxy) and benzoyloxy, cyano, isocyano, thiocyanato, isothiocyanato, nitro, NR'R'', -NHCOR', -NHCONR'R'', -CONR'R'', -COOR', -SO₂R', -OSO₂R', -COR', -CR'=NR'' or -N=CR'R'' in which R' and R'' are independently hydrogen, C₁₋₄ alkyl, halo(C₁₋₄)alkyl, C₁₋₄ alkoxy, halo-(C₁₋₄)alkoxy, C₁₋₄ alkylthio, C₃₋₆ cycloalkyl, C₃₋₆ cycloalkyl(C₁₋₄)alkyl, phenyl or benzyl, the phenyl and benzyl groups being optionally substituted with halogen, C₁₋₄ alkyl or C₁₋₄ alkoxy.

Substituents which may be present in the aryl or heteroaryl rings of any of the foregoing substituents include one or more of the following: halo, hydroxy, mercapto, C₁₋₄ alkyl, C₂₋₄, alkenyl, C₂₋₄ alkynyl, C₁₋₄ alkoxy, C₂₋₄ alkenyloxy, C₃₋₄ alkynyloxy, halo-(C₁₋₄)alkyl, halo(C₁₋₄)alkoxy, C₁₋₄ alkylthio, halo(C₁₋₄)alkylthio, hydroxy(C₁₋₄)alkyl, C₁₋₄alkoxy(C₁₋₄)alkyl, C₃₋₆ cycloalkyl, C₃₋₆ cycloalkyl(C₁₋₄)alkyl, alkanoyloxy, phenoxy, benzyloxy, benzoyloxy, cyano, isocyano, thiocyanato, isothiocyanato, nitro, -NR'R'', -NHCOR', -NHCONR'R'', -CONR'R'', -COOR', -SO₂R', -OSO₂R', -COR', -CR'=NR'' or -N=CR'R'', in which R' and R'' have the meanings given above.

Typically R is H, halo or C₁₋₄ alkyl. Usually it is methyl or chloro.

When one of X or Y is aryloxy, arylthio, heteroaryloxy, heteroarylthio, aryl(C₁₋₄)-alkoxy, heteroaryl(C₁₋₄)alkoxy, aryl(C₁₋₄)alkylthio, heteroaryl(C₁₋₄)alkylthio, arylamino,

aryl(C₁₋₈ alkyl)amino, heteroarylamino, heteroaryl(C₁₋₈ alkyl)amino, aryl(C₁₋₄)alkylamino, aryl(C₁₋₄)alkyl(C₁₋₈ alkyl)amino, heteroaryl(C₁₋₄)alkylamino or heteroaryl(C₁₋₄)alkyl(C₁₋₈ alkyl)amino the other is suitably halo, C₁₋₈ alkoxy, C₁₋₈ alkylthio, C₁₋₈ alkylamino, di(C₁₋₈)-alkylamino, or, in the case of Y, hydroxy.

5 In another aspect the invention provides the use as a plant fungicide of a compound of the general formula (I) wherein R is H, halo, C₁₋₈ alkyl or cyano; X is halo, C₁₋₈ alkoxy, C₁₋₈ alkylthio, C₁₋₈ alkylamino or di(C₁₋₈)alkylamino and Y is aryloxy, arylthio, heteroaryloxy, heteroarylthio, aryl(C₁₋₄)alkoxy, heteroaryl(C₁₋₄)alkoxy, aryl(C₁₋₄)alkylthio, heteroaryl(C₁₋₄)-alkylthio, C₁₋₈ alkylamino, C₂₋₈ alkenylamino, C₂₋₈ alkynylamino, di(C₁₋₈)alkylamino,
 10 arylamino, aryl(C₁₋₈ alkyl)amino, heteroarylamino, heteroaryl(C₁₋₈ alkyl)amino, aryl(C₁₋₄)-alkylamino, aryl(C₁₋₄)alkyl(C₁₋₈ alkyl)amino, heteroaryl(C₁₋₄)alkylamino, heteroaryl(C₁₋₄)-alkyl(C₁₋₈ alkyl)amino, morpholino or piperidino; any of the foregoing alkyl moieties being optionally substituted with halo and any of the foregoing aryl or heteroaryl groups being optionally substituted with halo, C₁₋₄ alkyl, C₁₋₄ alkoxy, halo(C₁₋₄)alkyl, halo(C₁₋₄)alkoxy,
 15 cyano, nitro, amino, C₁₋₄ alkylamino or di(C₁₋₄)alkylamino. In this aspect, R is typically halo or C₁₋₄ alkyl and X is typically halo (especially bromo), C₁₋₄ alkoxy or C₁₋₄ alkylthio. Aryl is usually phenyl and heteroaryl is, for example, pyridyl, pyrimidinyl, thienyl or imidazolyl. Typically Y is C₁₋₄ alkylamino, halo(C₁₋₄)alkylamino, C₂₋₄ alkenylamino, halo(C₂₋₄)-alkenylamino, C₂₋₄ alkynylamino, halo(C₂₋₄)alkynylamino, benzyloxy, benzylamino,
 20 heteroaryl(C₁₋₃)alkylamino where the heteroaryl moiety is, for example, pyridyl, thienyl or imidazolyl and the phenyl moieties of the benzyl groups and the heteroaryl moieties are optionally substituted with halo, C₁₋₄ alkyl, C₁₋₄ alkoxy, halo(C₁₋₄)alkyl, halo(C₁₋₄)alkoxy, cyano or nitro.

In yet another aspect the invention provides the use as a plant fungicide of a
 25 compound of the general formula (I) wherein R is H, halo, C₁₋₈ alkyl or cyano X is aryloxy, arylthio, heteroaryloxy, heteroarylthio, aryl(C₁₋₄)alkoxy, heteroaryl(C₁₋₄)alkoxy, aryl(C₁₋₄)alkylthio, heteroaryl(C₁₋₄)alkylthio, C₁₋₈ alkylamino, C₂₋₈ alkenylamino, C₂₋₈ alkynylamino, di(C₁₋₈)alkylamino, arylamino, aryl(C₁₋₈ alkyl)amino, heteroarylamino, heteroaryl(C₁₋₈ alkyl)amino, aryl(C₁₋₄)alkylamino, aryl(C₁₋₄)alkyl(C₁₋₈ alkyl)amino, heteroaryl(C₁₋₄)alkylamino, or heteroaryl(C₁₋₄)alkyl(C₁₋₈ alkyl)amino; and Y is halo, hydroxy, C₁₋₈ alkoxy, C₁₋₈ alkylthio, C₁₋₈ alkylamino or di(C₁₋₈)alkylamino; any of the foregoing alkyl moieties
 30 being optionally substituted with halo and any of the foregoing aryl or heteroaryl groups

being optionally substituted with halo, C₁₋₄ alkyl, C₁₋₄ alkoxy, halo(C₁₋₄)alkyl, halo(C₁₋₄)alkoxy, cyano, nitro, amino, C₁₋₄ alkylamino or di(C₁₋₄)alkylamino. In this aspect, R is typically halo or C₁₋₄ alkyl and Y is typically halo (especially chloro), hydroxy, C₁₋₄ alkylamino or halo(C₁₋₄)alkylamino. Aryl is usually phenyl and heteroaryl is, for example,
5 pyridyl, pyrimidinyl, thienyl or imidazolyl. Typically X is phenylthio or heteroarylthio where the heteroaryl moiety is, for example, pyridyl, thienyl or imidazolyl and the phenyl and heteroaryl moieties are optionally substituted with halo, C₁₋₄ alkyl, C₁₋₄ alkoxy, halo(C₁₋₄)alkyl, halo(C₁₋₄)alkoxy, cyano or nitro.

In yet another aspect the invention provides the use as a plant fungicide of a
10 compound of the general formula (I) wherein R is halo (e.g. chloro); X is phenoxy, phenylthio, heteroaryloxy (e.g. pyridyloxy and pyrimidinylloxy), heteroarylthio (e.g. pyridinylthio and pyrimidinylthio), morpholino or piperidino; and Y is C₁₋₈ alkylamino, C₂₋₈ alkenylamino, C₂₋₈ alkynylamino, di(C₁₋₈)alkylamino, di(C₂₋₈)alkenylamino, di(C₂₋₈)alkynylamino, C₂₋₈ alkenyl(C₁₋₈)alkylamino or C₂₋₈
15 alkenyl(C₁₋₈)alkylamino; any of the foregoing alkyl, alkenyl, alkynyl, phenyl, heteroaryl, morpholino or piperidino groups or moieties being optionally substituted. Halo, especially fluoro, is a typical substituent of alkyl, alkenyl and alkynyl and halo (e.g. chloro and fluoro), C₁₋₄ alkyl, halo(C₁₋₄)alkyl (e.g. trifluoromethyl), C₁₋₄ alkoxy, halo(C₁₋₄)alkoxy (e.g. trifluoromethoxy) and nitro are typical substituents of phenyl and heteroaryl groups.
20 Exemplary values of Y are 2,2,2-trifluoro-1-methylethylamino and *N*-ethyl-2-methylallylamino.

In yet another aspect the invention provides the use as a plant fungicide of a compound of the general formula (I) wherein R is halo (e.g. chloro); X is phenylthio, heteroaryloxy (e.g. pyridyloxy and pyrimidinylloxy) or heteroarylthio (e.g. pyridinylthio and
25 pyrimidinylthio); and Y is halo (e.g. chloro); any of the foregoing phenyl or heteroaryl moieties being optionally substituted, for example, with the substituents described in the previous paragraph.

The invention also includes those compounds of general formula (I) that are novel. Thus in yet another aspect the invention provides a compound of general formula (I) wherein
30 R is H, halo, C₁₋₈ alkyl or cyano; X and Y are independently halo, C₁₋₈ alkoxy, C₁₋₈ alkylthio, aryloxy, arylthio, heteroaryloxy, heteroarylthio, aryl(C₁₋₄)alkoxy, heteroaryl(C₁₋₄)alkoxy, aryl(C₁₋₄)alkylthio, heteroaryl(C₁₋₄)alkylthio, C₁₋₈ alkylamino, C₂₋₈ alkenylamino, C₂₋₈

- alkynylamino, di(C₁₋₈)alkylamino, arylamino, aryl(C₁₋₈ alkyl)amino, heteroarylamino, heteroaryl(C₁₋₈ alkyl)amino, aryl(C₁₋₄)alkylamino, aryl(C₁₋₄)alkyl(C₁₋₈ alkyl)amino, heteroaryl(C₁₋₄)alkylamino or heteroaryl(C₁₋₄)alkyl (C₁₋₈ alkyl)amino or Y is hydroxy, morpholino or piperidino; any of the foregoing alkyl, alkenyl, alkynyl, aryl, heteroaryl, morpholino or piperidino groups or moieties being optionally substituted; provided that when X is other than halo, R and Y are not both halo, that when X is bromo and R is methyl, Y is not diethylamino or 3-(diethylamino)-propylamino, that when X is chloro and R is methyl, Y is not benzylamino and that when X is bromo or chloro and R is H or methyl, Y is not chloro or hydroxy.
- More specifically, the invention includes a compound of the general formula (I) wherein R is H, halo, C₁₋₈ alkyl or cyano; X is halo, C₁₋₈ alkylthio, arylthio, heteroaryloxy, heteroarylthio, aryl(C₁₋₄)alkylthio, heteroaryl(C₁₋₄)alkylthio, C₁₋₈ alkylamino, C₂₋₈ alkenylamino, C₂₋₈ alkynylamino, di(C₁₋₈)alkylamino, arylamino, aryl(C₁₋₈ alkyl)amino, heteroarylamino, heteroaryl(C₁₋₈ alkyl)amino, aryl(C₁₋₄)alkylamino, aryl(C₁₋₄)alkyl(C₁₋₈ alkyl)amino, heteroaryl(C₁₋₄)alkylamino or heteroaryl(C₁₋₄)alkyl (C₁₋₈ alkyl)amino; and Y is halo, hydroxy, C₁₋₈ alkoxy, C₁₋₈ alkylthio, aryloxy, arylthio, heteroaryloxy, heteroarylthio, aryl(C₁₋₄)alkoxy, heteroaryl(C₁₋₄)alkoxy, aryl(C₁₋₄)alkylthio, heteroaryl(C₁₋₄)alkylthio, C₁₋₈ alkylamino, C₂₋₈ alkenylamino, C₂₋₈ alkynylamino, di(C₁₋₈)alkylamino, arylamino, aryl(C₁₋₈ alkyl)amino, heteroarylamino, heteroaryl(C₁₋₈ alkyl)amino, aryl(C₁₋₄)alkylamino, aryl(C₁₋₄)alkyl(C₁₋₈ alkyl)amino, heteroaryl(C₁₋₄)alkylamino or heteroaryl(C₁₋₄)alkyl (C₁₋₈ alkyl)amino, morpholino or piperidino; any of the foregoing alkyl, alkenyl, alkynyl, aryl, heteroaryl, morpholino or piperidino groups or moieties being optionally substituted; provided that when X is bromo and R is methyl, Y is not diethylamino or 3-(diethylamino)-propylamino, that when X is chloro and R is methyl, Y is not benzylamino and that when X is bromo or chloro and R is H or methyl, Y is not chloro or hydroxy.

The invention also includes a compound of the general formula (I) wherein R is halo (e.g. chloro); X is phenoxy, phenylthio, heteroaryloxy (e.g. pyridyloxy and pyrimidinylloxy), heteroarylthio (e.g. pyridinylthio and pyrimidinylthio), morpholino or piperidino; and Y is C₁₋₈ alkylamino, C₂₋₈ alkenylamino, C₂₋₈ alkynylamino, di(C₁₋₈)alkylamino, di(C₂₋₈)alkenylamino, di(C₂₋₈)alkynylamino, C₂₋₈ alkenyl(C₂₋₈)alkynylamino C₂₋₈ alkynyl(C₁₋₈)alkylamino or C₂₋₈ alkenyl(C₁₋₈)alkylamino; any of the foregoing alkyl, alkenyl, alkynyl, phenyl, heteroaryl, morpholino or piperidino groups or moieties being optionally substituted.

Halo, especially fluoro, is a typical substituent of alkyl, alkenyl and alkynyl and halo (e.g. chloro and fluoro), C₁₋₄ alkyl, halo(C₁₋₄)alkyl (e.g. trifluoromethyl), C₁₋₄ alkoxy, halo(C₁₋₄)alkoxy (e.g. trifluoromethoxy) and nitro are typical substituents of phenyl and heteroaryl groups. Exemplary values of Y are 2,2,2-trifluoro-1-methylethylamino and *N*-ethyl-2-methylallylamino.

The invention further includes a compound of the general formula (I) wherein R is halo (e.g. chloro); X is phenylthio, heteroaryloxy (e.g. pyridyloxy and pyrimidinyloxy) or heteroarylthio (e.g. pyridinylthio and pyrimidinylthio; and Y is halo (e.g. chloro); any of the foregoing phenyl or heteroaryl moieties being optionally substituted, for example, with the substituents described in the previous paragraph.

The further definitions of compound (I) detailed above in relation to its use as a fungicide (including specified usual, typical, suitable and exemplary values), apply equally to the invention compounds themselves.

Compounds that form part of the invention are illustrated in Table 1 below. The compounds have the general formula (I) with the values of R, X and Y given in the table.

Table 1

Compound No.	R	X	Y	Melting Point (°C)	Mass Ion (M ⁺ /M+1 ⁺)
1	CH ₃	Br	NHCH(CH ₃) ₂		270
2	CH ₃	Br	NHCH ₂ CF ₃		310
3	CH ₃	S-4-F-phenyl	Cl		295
4	CH ₃	S-5-CF ₃ -pyrid-2-yl	OH		328
5	CH ₃	SCH ₃	NHCH ₂ CF ₃		278
6	CH ₃	S-4-F-phenyl	NHCH(CH ₃) ₂	oil	318
7	CH ₃	I	OH		277
8	Cl	Br	Cl		267
9	CH ₃	Br	OCH ₂ -2,4,6-F ₃ -phenyl	202-4	374
10	CH ₃	Br	NHCH ₂ -4-F-phenyl		338
11	CH ₃	Br	Morpholino		299
12	CH ₃	Br	Piperidino		297
13	CH ₃	Br	OCH ₂ -3-CF ₃ -phenyl		388
14	CH ₃	Br	OCH ₂ -F ₅ -phenyl		410
15	CH ₃	Br	OCH ₂ -4-CN-phenyl		345
16	CH ₃	Br	OCH ₂ -3-NO ₂ -phenyl		365
17	CH ₃	Br	NH(CH ₂) ₃ -imidazol-1-yl		338
18	CH ₃	Br	NHCH ₂ -pyrid-2-yl		321
19	CH ₃	Br	NHCH ₂ C≡CH		268

20	CH ₃	Br	NHCH ₂ -thien-3-yl		326
21	Cl	S-4-F-phenyl	Cl		
22	Cl	Piperidino	(S)-NHCHCH ₃ CF ₃	127	
23	Cl	Piperidino	N(C ₂ H ₅)(CH ₂ C(CH ₃)=CH ₂)	133	
24	Cl	S-5-CF ₃ -pyrid-2-yl	Cl		
25	Cl	Morpholino	(S)-NHCHCH ₃ CF ₃	amorph	351
26	Cl	Morpholino	N(C ₂ H ₅)(CH ₂ C(CH ₃)=CH ₂)	amorph	337
27	Cl	S-3-NO ₂ -phenyl	Cl		
28	Cl	O-4-F-phenyl	(S)-NHCHCH ₃ CF ₃	156	
29	Cl	O-4-F-phenyl	N(C ₂ H ₅)(CH ₂ C(CH ₃)=CH ₂)	90	
30	Cl	S-3,4,5-F ₃ phenyl	Cl	218	
31	Cl	O-3,4,5-F ₃ -phenyl	(R)-NHCHCH ₃ CF ₃	128	
32	Cl	O-3,4,5-F ₃ -phenyl	N(C ₂ H ₅)(CH ₂ C(CH ₃)=CH ₂)	169	
33	Cl	S-2-NO ₂ -phenyl	Cl		
34	Cl	O-2-NO ₂ -phenyl	(S)-NHCHCH ₃ CF ₃	amorph	403
35	Cl	O-2-NO ₂ -phenyl	N(C ₂ H ₅)(CH ₂ C(CH ₃)=CH ₂)	amorph	489
36	Cl	S-4-MeO-phenyl	Cl		
37	Cl	O-4-MeO-phenyl	(S)-NHCHCH ₃ CF ₃		388
38	Cl	O-4-MeO-phenyl	N(C ₂ H ₅)(CH ₂ C(CH ₃)=CH ₂)		374
39	Cl	O-2-pyridyl	Cl		282
40	Cl	O-2-pyridyl	(S)-NHCHCH ₃ CF ₃		359
41	Cl	O-2-pyridyl	N(C ₂ H ₅)(CH ₂ C(CH ₃)=CH ₂)		345
42	Cl	S-2-F-phenyl	Cl		
43	Cl	O-2-F-phenyl	(S)-NHCHCH ₃ CF ₃		376
44	Cl	O-2-F-phenyl	N(C ₂ H ₅)(CH ₂ C(CH ₃)=CH ₂)		362
45	Cl	S-2-CH ₃ -phenyl	Cl		
46	Cl	O-2-CH ₃ -phenyl	(S)-NHCHCH ₃ CF ₃		372
47	Cl	O-2-CH ₃ -phenyl	N(C ₂ H ₅)(CH ₂ C(CH ₃)=CH ₂)		358
48	Cl	S-2,6-F ₂ -phenyl	Cl		
49	Cl	O-2,6-F ₂ -phenyl	(S)-NHCHCH ₃ CF ₃		394
50	Cl	O-2,6-F ₂ -phenyl	N(C ₂ H ₅)(CH ₂ C(CH ₃)=CH ₂)		380
51	Cl	O-2,4,6-F ₃ -phenyl	(S)-NHCHCH ₃ CF ₃	185	
52	Cl	O-2,4,6-F ₃ -phenyl	N(C ₂ H ₅)(CH ₂ C(CH ₃)=CH ₂)	203	
53	Cl	O-1-naphthyl	(S)-NHCHCH ₃ CF ₃		408
54	Cl	O-1-naphthyl	N(C ₂ H ₅)(CH ₂ C(CH ₃)=CH ₂)		394
55	Cl	O-2-MeO-5-Br-phenyl	(S)-NHCHCH ₃ CF ₃		466
56	Cl	O-2-MeO-5-Br-phenyl	N(C ₂ H ₅)(CH ₂ C(CH ₃)=CH ₂)		452
57	Cl	S-2-MeO-phenyl	(S)-NHCHCH ₃ CF ₃	123	
58	Cl	S-2-MeO-phenyl	N(C ₂ H ₅)(CH ₂ C(CH ₃)=CH ₂)	101	
59	Cl	S-phenyl	(S)-NHCHCH ₃ CF ₃		374
60	Cl	S-phenyl	N(C ₂ H ₅)(CH ₂ C(CH ₃)=CH ₂)		360
61	Cl	O-2-CF ₃ -phenyl	(S)-NHCHCH ₃ CF ₃		442
62	Cl	O-2-CF ₃ -phenyl	N(C ₂ H ₅)(CH ₂ C(CH ₃)=CH ₂)	101	
63	Me	Morpholino	(S)-NHCHCH ₃ CF ₃		

64	Me	Morpholino	$N(C_2H_5)(CH_2C(CH_3)=CH_2)$		
65	Me	S-3-NO ₂ -phenyl	Cl		
66	Me	O-4-F-phenyl	(S)-NHCHCH ₃ CF ₃		
67	Me	O-4-F-phenyl	$N(C_2H_5)(CH_2C(CH_3)=CH_2)$		
68	Me	S-3,4,5-F ₃ phenyl	Cl		
69	Me	O-3,4,5-F ₃ -phenyl	(R)-NHCHCH ₃ CF ₃		
70	Me	O-3,4,5-F ₃ -phenyl	$N(C_2H_5)(CH_2C(CH_3)=CH_2)$		
71	Me	S-2-NO ₂ -phenyl	Cl		
72	Me	O-2-NO ₂ -phenyl	(S)-NHCHCH ₃ CF ₃		
73	Me	O-2-NO ₂ -phenyl	$N(C_2H_5)(CH_2C(CH_3)=CH_2)$		
74	Me	S-4-MeO-phenyl	Cl		
75	Me	O-4-MeO-phenyl	(S)-NHCHCH ₃ CF ₃		
76	Me	O-4-MeO-phenyl	$N(C_2H_5)(CH_2C(CH_3)=CH_2)$		
77	Me	O-2-pyridyl	Cl		
78	Me	O-2-pyridyl	(S)-NHCHCH ₃ CF ₃		
79	Me	O-2-pyridyl	$N(C_2H_5)(CH_2C(CH_3)=CH_2)$		
80	Me	S-2-F-phenyl	Cl		
81	Me	O-2-F-phenyl	(S)-NHCHCH ₃ CF ₃		
82	Me	O-2-F-phenyl	$N(C_2H_5)(CH_2C(CH_3)=CH_2)$		
83	Me	S-2-CH ₃ -phenyl	Cl		
84	Me	O-2-CH ₃ -phenyl	(S)-NHCHCH ₃ CF ₃		
85	Me	O-2-CH ₃ -phenyl	$N(C_2H_5)(CH_2C(CH_3)=CH_2)$		
86	Me	S-2,6-F ₂ -phenyl	Cl		
87	Me	O-2,6-F ₂ -phenyl	(S)-NHCHCH ₃ CF ₃		
88	Me	O-2,6-F ₂ -phenyl	$N(C_2H_5)(CH_2C(CH_3)=CH_2)$		
89	Me	O-2,4,6-F ₃ -phenyl	(S)-NHCHCH ₃ CF ₃		
90	Me	O-2,4,6-F ₃ -phenyl	$N(C_2H_5)(CH_2C(CH_3)=CH_2)$		
91	Cl	Piperidino	(S)-NHCHCH ₃ CF ₃		
92	Cl	Piperidino	$N(C_2H_5)(CH_2C(CH_3)=CH_2)$		
93	Cl	O-2-MeO-phenyl	(S)-NHCHCH ₃ CF ₃		
94	Cl	O-2-MeO-phenyl	$N(C_2H_5)(CH_2C(CH_3)=CH_2)$		
95	Cl	O-2,4,5-F ₃ -phenyl	(S)-NHCHCH ₃ CF ₃		
96	Cl	O-2,4,5-F ₃ -phenyl	$N(C_2H_5)(CH_2C(CH_3)=CH_2)$		
97	Cl	S-2,4,5-F ₃ -phenyl	(S)-NHCHCH ₃ CF ₃		
98	Cl	S-2,4,5-F ₃ -phenyl	$N(C_2H_5)(CH_2C(CH_3)=CH_2)$		
99	Cl	S-2,4,6-F ₃ -phenyl	(S)-NHCHCH ₃ CF ₃		
100	Cl	S-2,4,6-F ₃ -phenyl	$N(C_2H_5)(CH_2C(CH_3)=CH_2)$		
101	Cl	O-2,6-F ₂ -phenyl	NHCH(CH ₃) ₂		
102	Cl	O-2,4,6-F ₃ -phenyl	NHCH(CH ₃) ₂		
103	Cl	O-2-naphthyl	NHCH(CH ₃) ₂		
104	Cl	O-2-MeO-5-Br-phenyl	NHCH(CH ₃) ₂		
105	Cl	S-2-MeO-phenyl	NHCH(CH ₃) ₂		
106	Cl	S-phenyl	NHCH(CH ₃) ₂		
107	Cl	O-2-CF ₃ -phenyl	NHCH(CH ₃) ₂		
108	Cl	Morpholino	NHCH(CH ₃) ₂		

109	Cl	S-3-NO ₂ -phenyl	NHCH(CH ₃) ₂		
110	Cl	O-4-F-phenyl	NHCH(CH ₃) ₂		
111	Cl	S-3,4,5-F ₃ phenyl	NHCH(CH ₃) ₂		
112	Cl	O-3,4,5-F ₃ -phenyl	NHCH(CH ₃) ₂		
113	Cl	S-2-NO ₂ -phenyl	NHCH(CH ₃) ₂		
114	Cl	O-2-NO ₂ -phenyl	NHCH(CH ₃) ₂		
115	Cl	S-4-MeO-phenyl	NHCH(CH ₃) ₂		
116	Cl	O-4-MeO-phenyl	NHCH(CH ₃) ₂		

The compounds of formula (I) may be prepared as outlined in Routes 1 to 6 below, in which R has the meaning given above and L is a leaving group such as halo. Y is shown as
 5 OR₁, NHR₁, NHR₂, NR₂R₃ or NR₃R₄ and X is shown as OR₁, SR₁, SR₂ or NR₁R₂, the values of R₁, R₂, R₃ and R₄ being derived from the meanings of X and Y given above. Hünig's base is *N,N*-diisopropylethylamine.

Thus, as shown in Route 1, compounds where Y is an amino-linked substituent (II), in which R is methyl, may be prepared by reacting a compound of general formula (III) with
 10 the appropriate primary amine R₁NH₂ or secondary amine R₁R₂NH conveniently in a solvent such as dimethyl sulphoxide at about 0°C in the presence of Hünig's base. The compound of general formula (III) may be prepared by treating a compound of general formula (IV) with phosphoryl chloride under reflux conditions. The compound of formula (IV) may be prepared by treating a compound of general formula (V) with liquid bromine at room temperature in,
 15 for example, glacial acetic acid. The compound of general formula (V) where R is methyl is commercially available.

Compounds where Y is an *O*-linked substituent (VI) may be prepared, as shown in Route 2, by reacting a compound of formula R₁-L with a compound of general formula (IV) in the presence of a suitable base

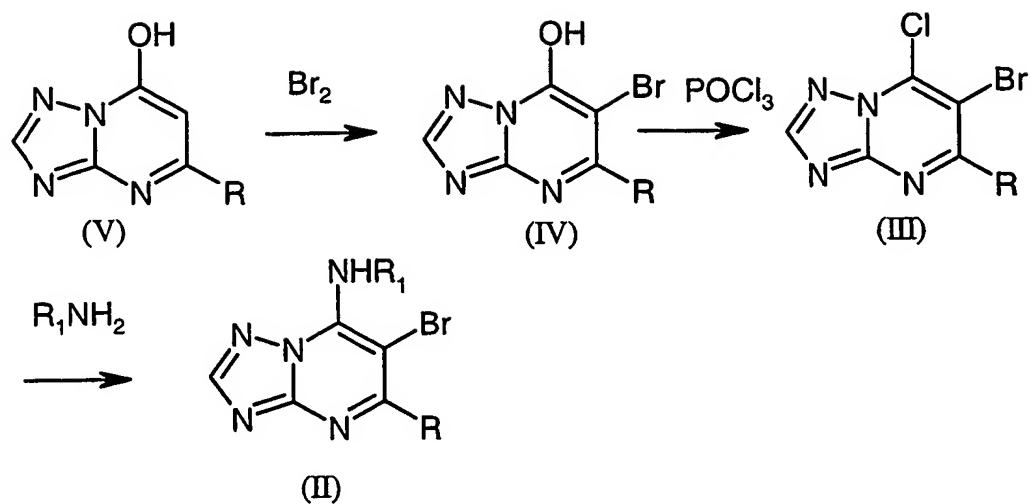
20 Compounds where X is a *S*-linked substituent and Y is an amino-linked substituent (VII) may be prepared, as shown in Route 3, by chlorinating a compound of general formula (VIII) with, for example, phosphoryl chloride followed by treatment with an amine R₂NH₂. The compound of general formula (VIII) may be prepared by reacting a compound of general formula (IV) with a thiol of formula R₁SH.

25 Compounds where X is a *S*-linked substituent and Y is an amino-linked substituent (IX) may also be prepared, as shown in Route 4, by reacting a compound of general formula (II) with a thiol of formula R₂SH.

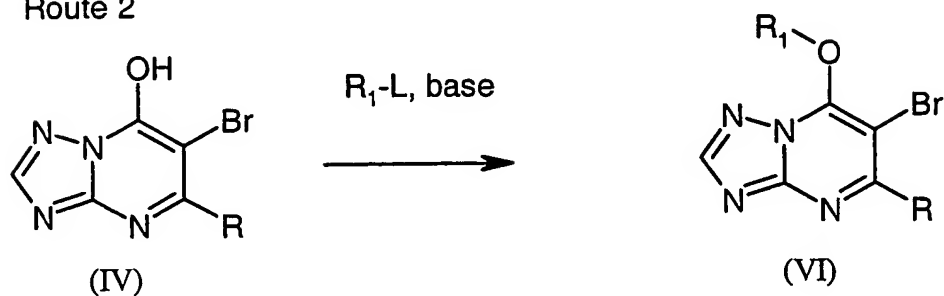
Compounds where X is an *O*-bridged substituent and Y is an amino-linked substituent (XI) may be prepared, as shown in Route 5, by chlorinating a compound of general formula (X) with, for example, phosphoryl chloride followed by treatment with an amine R_2R_3NH in DMF. The compound of general formula (X) may be prepared by reacting
5 a compound of general formula (IV) with a phenol of formula R_1OH in the presence of a suitable base like KF or K_2CO_3 .

Compounds where X is a *N*-bridged substituent and Y is an amino-linked substituent (XIII) may be prepared, as shown in Route 6, by chlorinating a compound of general formula (XII) with, for example, phosphoryl chloride followed by treatment with an amine R_3R_4NH
10 in DMF. The compound of general formula (XII) may be prepared by reacting a compound of general formula (IV) with an amine of formula R_3R_4NH in DMF.

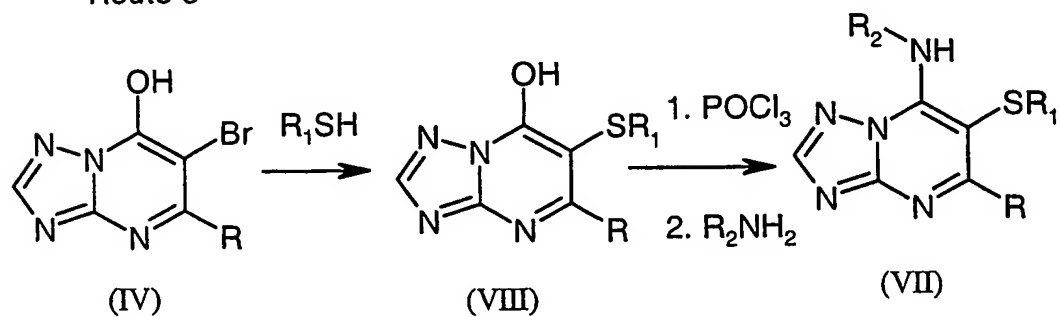
Route 1



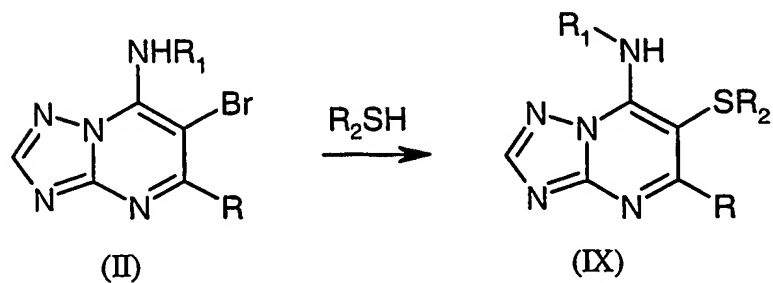
Route 2



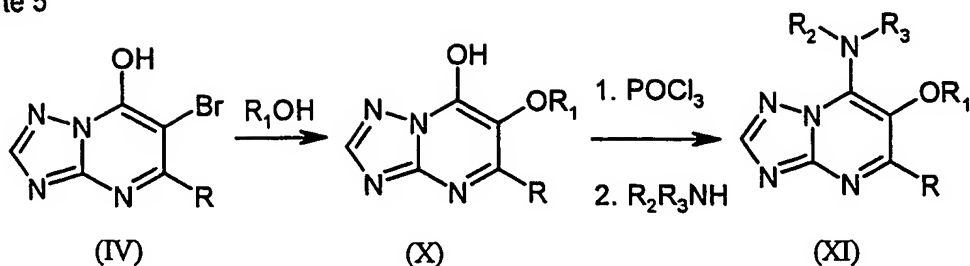
Route 3



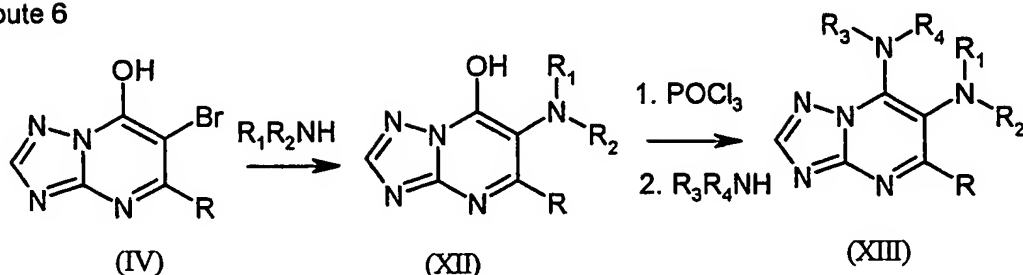
Route 4



Route 5



Route 6



Other compounds of the general formula (I) may be prepared by standard methods described in the literature from the commercially available 5-methyl-*s*-triazolo[1,5-*a*]pyrimidin-7-ol (compound (V) where R is methyl) or using compounds (II), (III), (IV), (VI) or
 5 (VIII) as intermediates. Alternatively, they may be prepared from intermediates described by Y. Makisumi in *Chem. Pharm. Bull.* (Tokyo), **9**, 801-808 & 808-814 by standard literature methods.

The compounds of formula (I) are active fungicides and may be used to control one or more of the following pathogens: *Pyricularia oryzae* (*Magnaporthe grisea*) on rice and wheat
 10 and other *Pyricularia* spp. on other hosts; *Puccinia trititica* (or *recondita*), *Puccinia striiformis* and other rusts on wheat, *Puccinia hordei*, *Puccinia striiformis* and other rusts on barley, and rusts on other hosts (for example turf, rye, coffee, pears, apples, peanuts, sugar beet, vegetables and ornamental plants); *Erysiphe cichoracearum* on cucurbits (for example melon); *Blumeria* (or *Erysiphe*) *graminis* (powdery mildew) on barley, wheat, rye and turf
 15 and other powdery mildews on various hosts, such as *Sphaerotheca macularis* on hops, *Sphaerotheca fusca* (*Sphaerotheca fuliginea*) on cucurbits (for example cucumber), *Leveillula taurica* on tomatoes, aubergine and green pepper, *Podosphaera leucotricha* on apples and *Uncinula necator* on vines; *Cochliobolus* spp., *Helminthosporium* spp., *Drechslera* spp. (*Pyrenophora* spp.), *Rhynchosporium* spp., *Mycosphaerella graminicola*
 20 (*Septoria tritici*) and *Phaeosphaeria nodorum* (*Stagonospora nodorum* or *Septoria nodorum*), *Pseudocercospora herpotrichoides* and *Gaeumannomyces graminis* on cereals

(for example wheat, barley, rye), turf and other hosts; *Cercospora arachidicola* and *Cercosporidium personatum* on peanuts and other *Cercospora* spp. on other hosts, for example sugar beet, bananas, soya beans and rice; *Botrytis cinerea* (grey mould) on tomatoes, strawberries, vegetables, vines and other hosts and other *Botrytis* spp. on other hosts;

5 *Alternaria* spp. on vegetables (for example carrots), oil-seed rape, apples, tomatoes, potatoes, cereals (for example wheat) and other hosts; *Venturia* spp. (including *Venturia inaequalis* (scab)) on apples, pears, stone fruit, tree nuts and other hosts; *Cladosporium* spp. on a range of hosts including cereals (for example wheat) and tomatoes; *Monilinia* spp. on stone fruit, tree nuts and other hosts; *Didymella* spp. on tomatoes, turf, wheat, cucurbits and other hosts;

10 *Phoma* spp. on oil-seed rape, turf, rice, potatoes, wheat and other hosts; *Aspergillus* spp. and *Aureobasidium* spp. on wheat, lumber and other hosts; *Ascochyta* spp. on peas, wheat, barley and other hosts; *Stemphylium* spp. (*Pleospora* spp.) on apples, pears, onions and other hosts; summer diseases (for example bitter rot (*Glomerella cingulata*), black rot or frog-eye leaf spot (*Botryosphaeria obtusa*), Brooks fruit spot (*Mycosphaerella pomi*), Cedar apple rust

15 (*Gymnosporangium juniperi-virginianae*), sooty blotch (*Gloeodes pomigena*), flyspeck (*Schizothyrium pomi*) and white rot (*Botryosphaeria dothidea*) on apples and pears; *Plasmopara viticola* on vines; other downy mildews, such as *Bremia lactucae* on lettuce, *Peronospora* spp. on soybeans, tobacco, onions and other hosts, *Pseudoperonospora humuli* on hops and *Pseudoperonospora cubensis* on cucurbits; *Pythium* spp. (including *Pythium*

20 *ultimum*) on turf and other hosts; *Phytophthora infestans* on potatoes and tomatoes and other *Phytophthora* spp. on vegetables, strawberries, avocado, pepper, ornamentals, tobacco, cocoa and other hosts; *Thanatephorus cucumeris* on rice and turf and other *Rhizoctonia* spp. on various hosts such as wheat and barley, peanuts, vegetables, cotton and turf; *Sclerotinia* spp. on turf, peanuts, potatoes, oil-seed rape and other hosts; *Sclerotium* spp. on turf, peanuts

25 and other hosts; *Gibberella fujikuroi* on rice; *Colletotrichum* spp. on a range of hosts including turf, coffee and vegetables; *Laetisaria fuciformis* on turf; *Mycosphaerella* spp. on bananas, peanuts, citrus, pecans, papaya and other hosts; *Diaporthe* spp. on citrus, soybean, melon, pears, lupin and other hosts; *Elsinoe* spp. on citrus, vines, olives, pecans, roses and other hosts; *Verticillium* spp. on a range of hosts including hops, potatoes and tomatoes;

30 *Pyrenopeziza* spp. on oil-seed rape and other hosts; *Oncobasidium theobromae* on cocoa causing vascular streak dieback; *Fusarium* spp., *Typhula* spp., *Microdochium nivale*, *Ustilago* spp., *Urocystis* spp., *Tilletia* spp. and *Claviceps purpurea* on a variety of hosts but

particularly wheat, barley, turf and maize; *Ramularia* spp. on sugar beet, barley and other hosts; post-harvest diseases particularly of fruit (for example *Penicillium digitatum*, *Penicillium italicum* and *Trichoderma viride* on oranges, *Colletotrichum musae* and *Gloeosporium musarum* on bananas and *Botrytis cinerea* on grapes); other pathogens on
5 vines, notably *Eutypa lata*, *Guignardia bidwellii*, *Phellinus igniarius*, *Phomopsis viticola*, *Pseudopeziza tracheiphila* and *Stereum hirsutum*; other pathogens on trees (for example *Lophodermium seeditiosum*) or lumber, notably *Cephaloascus fragrans*, *Ceratocystis* spp., *Ophiostoma piceae*, *Penicillium* spp., *Trichoderma pseudokoningii*, *Trichoderma viride*, *Trichoderma harzianum*, *Aspergillus niger*, *Leptographium lindbergi* and *Aureobasidium*
10 *pullulans*; and fungal vectors of viral diseases (for example *Polymyxa graminis* on cereals as the vector of barley yellow mosaic virus (BYMV) and *Polymyxa betae* on sugar beet as the vector of rhizomania).

A compound of formula (I) may move acropetally, basipetally or locally in plant tissue to be active against one or more fungi. Moreover, a compound of formula (I) may be
15 volatile enough to be active in the vapour phase against one or more fungi on the plant.

The invention therefore provides a method of combating or controlling phytopathogenic fungi which comprises applying a fungicidally effective amount of a compound of formula (I), or a composition containing a compound of formula (I), to a plant, to a seed of a plant, to the locus of the plant or seed or to soil or any other plant growth medium, e.g.
20 nutrient solution.

The term "plant" as used herein includes seedlings, bushes and trees. Furthermore, the fungicidal method of the invention includes protectant, curative, systemic, eradicant and antisporeulant treatments.

The compounds of formula (I) are preferably used for agricultural, horticultural and
25 turfgrass purposes in the form of a composition.

In order to apply a compound of formula (I) to a plant, to a seed of a plant, to the locus of the plant or seed or to soil or any other growth medium, a compound of formula (I) is usually formulated into a composition which includes, in addition to the compound of formula (I), a suitable inert diluent or carrier and, optionally, a surface active agent (SFA).
30 SFAs are chemicals that are able to modify the properties of an interface (for example, liquid/solid, liquid/air or liquid/liquid interfaces) by lowering the interfacial tension and thereby leading to changes in other properties (for example dispersion, emulsification and

wetting). It is preferred that all compositions (both solid and liquid formulations) comprise, by weight, 0.0001 to 95%, more preferably 1 to 85%, for example 5 to 60%, of a compound of formula (I). The composition is generally used for the control of fungi such that a compound of formula (I) is applied at a rate of from 0.1g to 10kg per hectare, preferably from 1g to 6kg per hectare, more preferably from 1g to 1kg per hectare.

When used in a seed dressing, a compound of formula (I) is used at a rate of 0.0001g to 10g (for example 0.001g or 0.05g), preferably 0.005g to 10g, more preferably 0.005g to 4g, per kilogram of seed.

In another aspect the present invention provides a fungicidal composition comprising a fungicidally effective amount of a compound of formula (I) and a suitable carrier or diluent therefor.

In a still further aspect the invention provides a method of combating and controlling fungi at a locus which comprises treating the fungi or the locus of the fungi with a fungicidally effective amount of a composition comprising a compound of formula (I).

The compositions can be chosen from a number of formulation types, including dustable powders (DP), soluble powders (SP), water soluble granules (SG), water dispersible granules (WG), wettable powders (WP), granules (GR) (slow or fast release), soluble concentrates (SL), oil miscible liquids (OL), ultra low volume liquids (UL), emulsifiable concentrates (EC), dispersible concentrates (DC), emulsions (both oil in water (EW) and water in oil (EO)), micro-emulsions (ME), suspension concentrates (SC), aerosols, fogging/smoke formulations, capsule suspensions (CS) and seed treatment formulations. The formulation type chosen in any instance will depend upon the particular purpose envisaged and the physical, chemical and biological properties of the compound of formula (I).

Dustable powders (DP) may be prepared by mixing a compound of formula (I) with one or more solid diluents (for example natural clays, kaolin, pyrophyllite, bentonite, alumina, montmorillonite, kieselguhr, chalk, diatomaceous earths, calcium phosphates, calcium and magnesium carbonates, sulphur, lime, flours, talc and other organic and inorganic solid carriers) and mechanically grinding the mixture to a fine powder.

Soluble powders (SP) may be prepared by mixing a compound of formula (I) with one or more water-soluble inorganic salts (such as sodium bicarbonate, sodium carbonate or magnesium sulphate) or one or more water-soluble organic solids (such as a polysaccharide) and, optionally, one or more wetting agents, one or more dispersing agents or a mixture of

said agents to improve water dispersibility/solubility. The mixture is then ground to a fine powder. Similar compositions may also be granulated to form water soluble granules (SG).

Wettable powders (WP) may be prepared by mixing a compound of formula (I) with one or more solid diluents or carriers, one or more wetting agents and, preferably, one or more dispersing agents and, optionally, one or more suspending agents to facilitate the dispersion in liquids. The mixture is then ground to a fine powder. Similar compositions may also be granulated to form water dispersible granules (WG).

Granules (GR) may be formed either by granulating a mixture of a compound of formula (I) and one or more powdered solid diluents or carriers, or from pre-formed blank granules by absorbing a compound of formula (I) (or a solution thereof, in a suitable agent) in a porous granular material (such as pumice, attapulgite clays, fuller's earth, kieselguhr, diatomaceous earths or ground corn cobs) or by adsorbing a compound of formula (I) (or a solution thereof, in a suitable agent) on to a hard core material (such as sands, silicates, mineral carbonates, sulphates or phosphates) and drying if necessary. Agents which are commonly used to aid absorption or adsorption include solvents (such as aliphatic and aromatic petroleum solvents, alcohols, ethers, ketones and esters) and sticking agents (such as polyvinyl acetates, polyvinyl alcohols, dextrans, sugars and vegetable oils). One or more other additives may also be included in granules (for example an emulsifying agent, wetting agent or dispersing agent).

Dispersible Concentrates (DC) may be prepared by dissolving a compound of formula (I) in water or an organic solvent, such as a ketone, alcohol or glycol ether. These solutions may contain a surface active agent (for example to improve water dilution or prevent crystallisation in a spray tank).

Emulsifiable concentrates (EC) or oil-in-water emulsions (EW) may be prepared by dissolving a compound of formula (I) in an organic solvent (optionally containing one or more wetting agents, one or more emulsifying agents or a mixture of said agents). Suitable organic solvents for use in ECs include aromatic hydrocarbons (such as alkylbenzenes or alkylnaphthalenes, exemplified by SOLVESSO 100, SOLVESSO 150 and SOLVESSO 200; SOLVESSO is a Registered Trade Mark), ketones (such as cyclohexanone or methylcyclohexanone), alcohols (such as benzyl alcohol, furfuryl alcohol or butanol), N-alkylpyrrolidones (such as N-methylpyrrolidone or N-octylpyrrolidone), dimethyl amides of fatty acids (such as C₈-C₁₀ fatty acid dimethylamide) and chlorinated hydrocarbons. An EC

product may spontaneously emulsify on addition to water, to produce an emulsion with sufficient stability to allow spray application through appropriate equipment. Preparation of an EW involves obtaining a compound of formula (I) either as a liquid (if it is not a liquid at room temperature, it may be melted at a reasonable temperature, typically below 70°C) or in solution (by dissolving it in an appropriate solvent) and then emulsifying the resultant liquid or solution into water containing one or more SFAs, under high shear, to produce an emulsion. Suitable solvents for use in EWs include vegetable oils, chlorinated hydrocarbons (such as chlorobenzenes), aromatic solvents (such as alkylbenzenes or alkylnaphthalenes) and other appropriate organic solvents that have a low solubility in water.

Microemulsions (ME) may be prepared by mixing water with a blend of one or more solvents with one or more SFAs, to produce spontaneously a thermodynamically stable isotropic liquid formulation. A compound of formula (I) is present initially in either the water or the solvent/SFA blend. Suitable solvents for use in MEs include those hereinbefore described for use in ECs or in EWs. An ME may be either an oil-in-water or a water-in-oil system (which system is present may be determined by conductivity measurements) and may be suitable for mixing water-soluble and oil-soluble pesticides in the same formulation. An ME is suitable for dilution into water, either remaining as a microemulsion or forming a conventional oil-in-water emulsion.

Suspension concentrates (SC) may comprise aqueous or non-aqueous suspensions of finely divided insoluble solid particles of a compound of formula (I). SCs may be prepared by ball or bead milling the solid compound of formula (I) in a suitable medium, optionally with one or more dispersing agents, to produce a fine particle suspension of the compound. One or more wetting agents may be included in the composition and a suspending agent may be included to reduce the rate at which the particles settle. Alternatively, a compound of formula (I) may be dry milled and added to water, containing agents hereinbefore described, to produce the desired end product.

Aerosol formulations comprise a compound of formula (I) and a suitable propellant (for example *n*-butane). A compound of formula (I) may also be dissolved or dispersed in a suitable medium (for example water or a water miscible liquid, such as *n*-propanol) to provide compositions for use in non-pressurised, hand-actuated spray pumps.

A compound of formula (I) may be mixed in the dry state with a pyrotechnic mixture to form a composition suitable for generating, in an enclosed space, a smoke containing the compound.

Capsule suspensions (CS) may be prepared in a manner similar to the preparation of
5 EW formulations but with an additional polymerisation stage such that an aqueous dispersion of oil droplets is obtained, in which each oil droplet is encapsulated by a polymeric shell and contains a compound of formula (I) and, optionally, a carrier or diluent therefor. The polymeric shell may be produced by either an interfacial polycondensation reaction or by a coacervation procedure. The compositions may provide for controlled release of the
10 compound of formula (I) and they may be used for seed treatment. A compound of formula (I) may also be formulated in a biodegradable polymeric matrix to provide a slow, controlled release of the compound.

A composition may include one or more additives to improve the biological performance of the composition (for example by improving wetting, retention or distribution
15 on surfaces; resistance to rain on treated surfaces; or uptake or mobility of a compound of formula (I)). Such additives include surface active agents, spray additives based on oils, for example certain mineral oils or natural plant oils (such as soy bean and rape seed oil), and blends of these with other bio-enhancing adjuvants (ingredients which may aid or modify the action of a compound of formula (I)).

20 A compound of formula (I) may also be formulated for use as a seed treatment, for example as a powder composition, including a powder for dry seed treatment (DS), a water soluble powder (SS) or a water dispersible powder for slurry treatment (WS), or as a liquid composition, including a flowable concentrate (FS), a solution (LS) or a capsule suspension (CS). The preparations of DS, SS, WS, FS and LS compositions are very similar to those of,
25 respectively, DP, SP, WP, SC and DC compositions described above. Compositions for treating seed may include an agent for assisting the adhesion of the composition to the seed (for example a mineral oil or a film-forming barrier).

Wetting agents, dispersing agents and emulsifying agents may be SFAs of the cationic, anionic, amphoteric or non-ionic type.

30 Suitable SFAs of the cationic type include quaternary ammonium compounds (for example cetyltrimethyl ammonium bromide), imidazolines and amine salts.

Suitable anionic SFAs include alkali metals salts of fatty acids, salts of aliphatic monoesters of sulphuric acid (for example sodium lauryl sulphate), salts of sulphonated aromatic compounds (for example sodium dodecylbenzenesulphonate, calcium dodecylbenzenesulphonate, butylnaphthalene sulphonate and mixtures of sodium di-
5 *isopropyl*- and tri-*isopropyl*-naphthalene sulphonates), ether sulphates, alcohol ether sulphates (for example sodium laureth-3-sulphate), ether carboxylates (for example sodium laureth-3-carboxylate), phosphate esters (products from the reaction between one or more fatty alcohols and phosphoric acid (predominately mono-esters) or phosphorus pentoxide (predominately di-esters), for example the reaction between lauryl alcohol and
10 tetraphosphoric acid; additionally these products may be ethoxylated), sulphosuccinamates, paraffin or olefine sulphonates, taurates and lignosulphonates.

Suitable SFAs of the amphoteric type include betaines, propionates and glycines.

Suitable SFAs of the non-ionic type include condensation products of alkylene oxides, such as ethylene oxide, propylene oxide, butylene oxide or mixtures thereof, with fatty
15 alcohols (such as oleyl alcohol or cetyl alcohol) or with alkylphenols (such as octylphenol, nonylphenol or octylcresol); partial esters derived from long chain fatty acids or hexitol anhydrides; condensation products of said partial esters with ethylene oxide; block polymers (comprising ethylene oxide and propylene oxide); alkanolamides; simple esters (for example fatty acid polyethylene glycol esters); amine oxides (for example lauryl dimethyl amine
20 oxide); and lecithins.

Suitable suspending agents include hydrophilic colloids (such as polysaccharides, polyvinylpyrrolidone or sodium carboxymethylcellulose) and swelling clays (such as bentonite or attapulgite).

A compound of formula (I) may be applied by any of the known means of applying
25 fungicidal compounds. For example, it may be applied, formulated or unformulated, to any part of the plant, including the foliage, stems, branches or roots, to the seed before it is planted or to other media in which plants are growing or are to be planted (such as soil surrounding the roots, the soil generally, paddy water or hydroponic culture systems), directly or it may be sprayed on, dusted on, applied by dipping, applied as a cream or paste
30 formulation, applied as a vapour or applied through distribution or incorporation of a composition (such as a granular composition or a composition packed in a water-soluble bag) in soil or an aqueous environment.

A compound of formula (I) may also be injected into plants or sprayed onto vegetation using electrodynamic spraying techniques or other low volume methods, or applied by land or aerial irrigation systems.

Compositions for use as aqueous preparations (aqueous solutions or dispersions) are generally supplied in the form of a concentrate containing a high proportion of the active ingredient, the concentrate being added to water before use. These concentrates, which may include DCs, SCs, ECs, EWs, MEs SGs, SPs, WPs, WGs and CSs, are often required to withstand storage for prolonged periods and, after such storage, to be capable of addition to water to form aqueous preparations which remain homogeneous for a sufficient time to enable them to be applied by conventional spray equipment. Such aqueous preparations may contain varying amounts of a compound of formula (I) (for example 0.0001 to 10%, by weight) depending upon the purpose for which they are to be used.

A compound of formula (I) may be used in mixtures with fertilisers (for example nitrogen-, potassium- or phosphorus-containing fertilisers). Suitable formulation types include granules of fertiliser. The mixtures suitably contain up to 25% by weight of the compound of formula (I).

The invention therefore also provides a fertiliser composition comprising a fertiliser and a compound of formula (I).

The compositions of this invention may contain other compounds having biological activity, for example micronutrients or compounds having similar or complementary fungicidal activity or which possess plant growth regulating, herbicidal, insecticidal, nematocidal or acaricidal activity.

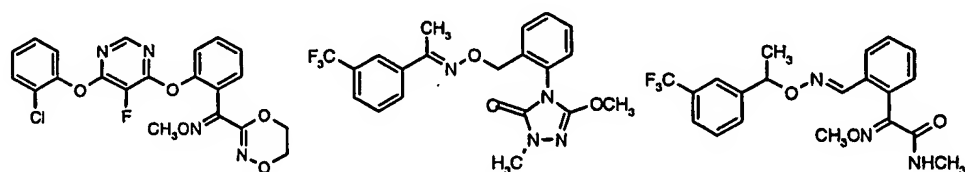
By including another fungicide, the resulting composition may have a broader spectrum of activity or a greater level of intrinsic activity than the compound of formula (I) alone. Further the other fungicide may have a synergistic effect on the fungicidal activity of the compound of formula (I).

The compound of formula (I) may be the sole active ingredient of the composition or it may be admixed with one or more additional active ingredients such as a pesticide, fungicide, synergist, herbicide or plant growth regulator where appropriate. An additional active ingredient may: provide a composition having a broader spectrum of activity or increased persistence at a locus; synergise the activity or complement the activity (for example by increasing the speed of effect or overcoming repellency) of the compound of

formula (I); or help to overcome or prevent the development of resistance to individual components. The particular additional active ingredient will depend upon the intended utility of the composition.

Examples of fungicidal compounds which may be included in the composition of the invention are AC 382042 (*N*-(1-cyano-1,2-dimethylpropyl)-2-(2,4-dichlorophenoxy) propionamide), acibenzolar-*S*-methyl, alanycarb, aldimorph, anilazine, azaconazole, azafenidin, azoxystrobin, benalaxyl, benomyl, biloxazol, bitertanol, blasticidin *S*, bromuconazole, bupirimate, captafol, captan, carbendazim, carbendazim chlorhydrate, carboxin, carpropamid, carvone, CGA 41396, CGA 41397, chinomethionate, chlorbenzthiazole, chlorothalonil, chlorozoline, clozylacon, copper containing compounds such as copper oxychloride, copper oxyquinolate, copper sulphate, copper tallate, and Bordeaux mixture, cyamidazosulfamid, cyflufenamid, cymoxanil, cyproconazole, cyprodinil, debacarb, di-2-pyridyl disulphide 1,1'-dioxide, dichlofluanid, diclocymet, diclomezine, dicloran, didecyl dimethyl ammonium chloride, diethofencarb, difenoconazole, difenzoquat, diflumetorim, *O,O*-di-*iso*-propyl-*S*-benzyl thiophosphate, dimefluazole, dimetconazole, dimethirimol, dimethomorph, dimoxystrobin, diniconazole, dinocap, dithianon, dodecyl dimethyl ammonium chloride, dodemorph, dodine, doguadine, edifenphos, epoxiconazole, ethaboxam, ethirimol, ethyl (*Z*)-*N*-benzyl-*N*-([methyl(methyl-thioethylideneaminooxycarbonyl)amino]thio)- β -alaninate, etridiazole, famoxadone, fenamidone, fenarimol, fenbuconazole, fenfuram, fenhexamid, fenpiclonil, fenpropidin, fenpropimorph, fentin acetate, fentin hydroxide, ferbam, ferimzone, fluazinam, fludioxonil, flumetover, flumorph, fluoroimide, fluoxastrobin, fluquinconazole, flusilazole, flusulfamide, flutolanil, flutriafol, folpet, fosetyl-aluminium, fuberidazole, furalaxyl, furametpyr, guazatine, hexaconazole, hydroxyisoxazole, hymexazole, imazalil, imibenconazole, iminoctadine, iminoctadine triacetate, ipconazole, iprobenfos, iprodione, iprovalicarb, isopropanyl butyl carbamate, isoprothiolane, kasugamycin, kresoxim-methyl, LY186054, LY211795, LY 248908, mancozeb, maneb, mefenoxam, mepanipyrim, mepronil, metalaxyl, metconazole, metiram, metiram-zinc, metominostrobin, metrafenone, MON65500 (*N*-allyl-4,5-dimethyl-2-trimethylsilylthiophene-3-carboxamide), myclobutanil, NTN0301, neoasozin, nickel dimethyldithiocarbamate, nicobifen, nitrothale-isopropyl, nuarimol, ofurace, organomercury compounds, oxadixyl, oxasulfuron, oxolinic acid, oxpoconazole, oxycarboxin, pefurazoate, penconazole, pencycuron, phenazin oxide, phosphorus acids, phthalide, picoxystrobin, polyoxin D, polyram, probenazole, prochloraz, procymidone,

propamocarb, propamocarb hydrochloride, propiconazole, propineb, propionic acid, prothioconazole, pyraclostrobin, pyrazophos, pyrifenoxy, pyrimethanil, pyroquilon, pyroxyfur, pyrrolnitrin, quaternary ammonium compounds, quinomethionate, quinoxifen, quintozone, sipconazole, sodium pentachlorophenate, spiroxamine, streptomycin, sulphur, tebuconazole, 5 tecloftalam, tecnazene, tetraconazole, thiabendazole, thifluzamide, 2-(thiocyanomethylthio)-benzothiazole, thiophanate-methyl, thiram, tiadinil, timibenconazole, tolclofos-methyl, tolylfluanid, triadimefon, triadimenol, triazbutil, triazoxide, tricyclazole, tridemorph, trifloxystrobin, triflumizole, triforine, triticonazole, validamycin A, vapam, vinclozolin, XRD-563, zineb, ziram, zoxamide and compounds of the formulae:



10

The compounds of formula (I) may be mixed with soil, peat or other rooting media for the protection of plants against seed-borne, soil-borne or foliar fungal diseases.

Some mixtures may comprise active ingredients which have significantly different physical, chemical or biological properties such that they do not easily lend themselves to the same conventional formulation type. In these circumstances other formulation types may be prepared. For example, where one active ingredient is a water insoluble solid and the other a water insoluble liquid, it may nevertheless be possible to disperse each active ingredient in the same continuous aqueous phase by dispersing the solid active ingredient as a suspension (using a preparation analogous to that of an SC) but dispersing the liquid active ingredient as an emulsion (using a preparation analogous to that of an EW). The resultant composition is a suspoemulsion (SE) formulation.

The invention is illustrated by the following Examples in which the following abbreviations are used:

ml = millilitres

nmr = nuclear magnetic resonance

g = grammes

DMSO = dimethyl sulphoxide

ppm = parts per million

DMF = *N,N*-dimethylformamide M^+ = mass ion

HPLC = high performance liquid chromatography

EXAMPLE 1

This Example illustrates the preparation of 5-methyl-6-bromo-7-trifluoroethylamino-s-1,2,4-triazolo[1,5-a]pyrimidine (Compound No. 2, Table 1)

Stage 1

5 A solution of bromine (4.1ml) in glacial acetic acid (20ml) was added dropwise to a solution of 5-methyl-s-triazolo[1,5-a]pyrimidin-7-ol (10.0g) in glacial acetic acid (80ml) with stirring at room temperature. After complete addition, the solution was stirred at room temperature for 3 hours. The solid was separated by filtration, washed with ethanol and air dried to give 5-methyl-6-bromo-s-triazolo[1,5-a]pyrimidin-7-ol (14.8g, 98% yield) as a pale
10 yellow solid.

^1H nmr δ 2.40 (3H,s), 3.80 (1H, bs), 8.20 (1H, s) ppm.

Stage 2

Phosphoryl chloride (25ml) was added dropwise, with caution, to 5-methyl-6-bromo-s-triazolo[1,5-a]pyrimidin-7-ol (5.0g). After complete addition the mixture was refluxed for
15 24 hours, cooled to room temperature and poured carefully with stirring onto crushed ice. The resulting red solution was extracted with chloroform, washed with water, dried and the solvent removed to give 5-methyl-6-bromo-7-chloro-s-triazolo[1,5-a]pyrimidine (3.60g, 70% yield) as an orange solid.

^1H nmr δ 2.90 (3H, s), 8.50 (1H, s) ppm.

20 Stage 3

2,2,2-Trifluoroethylamine (3.2ml) was added dropwise to a solution of 5-methyl-6-bromo-7-chloro-s-triazolo[1,5-a]pyrimidine (2.5g) and Hünig's base (2.6ml) in dry DMSO (25ml) at 0°C. The reaction was stirred for 3 days at room temperature, poured into ice cold water and extracted with ether. The ether extracts were washed with water, dried over
25 anhydrous magnesium sulphate and the ether removed to give the title compound (1.35g, 43% yield) as a yellow solid ($M^+ = 310$).

^1H nmr δ 2.80 (3H, s), 5.00 (2H, m), 6.00 (1H,m), 8.30 (1H, s) ppm.

EXAMPLE 2

This Example illustrates the preparation of 5-methyl-6-bromo-7-isopropylamino-s-1,2,4-triazolo[1,5-a]pyrimidine (Compound No. 1, Table 1)
30

Isopropylamine (0.75ml) was added dropwise to a solution of 5-methyl-6-bromo-7-chloro-s-triazolo[1,5-a]pyrimidine (1.0g) (prepared as described in Example 1, Stage 2) and

Hünig's base (1.0ml) in dry DMSO (10ml) at 0°C. The reaction mixture was stirred at room temperature for 2.5 hours, poured into ice-cold water and extracted with ether. The ether extracts were washed with water, dried over anhydrous magnesium sulphate and the ether removed to give the title compound (0.7g, 65% yield) as a yellow powder ($M^+ = 270$).

5 ^1H nmr δ 1.4 (6H, d), 2.7 (3H, s), 5.3 (1H, m), 5.7 (1H, d), 8.2 (1H, s) ppm.

EXAMPLE 3

This Example illustrates the preparation of 5-methyl-6-(4-fluoro-(phenylthio)-7-isopropylamino-s-1,2,4-triazolo[1,5-a]pyrimidine (Compound No. 6, Table 1)

A mixture of 5-Methyl-6-bromo-7-isopropylamino-s-1,2,4-triazolo[1,5-a]pyrimidine
10 (0.230g) (prepared as described in Example 2), 4-fluorothiophenol (0.128g) and anhydrous potassium carbonate (0.138g) in ethylene glycol (6ml) was stirred under a nitrogen atmosphere at 150°C for 3 hours. The reaction mixture was cooled to room temperature, poured into ice water and extracted with ethyl acetate. The ether extracts were washed with water, dried over anhydrous magnesium sulphate and the solvent removed to give a yellow
15 oil which was purified by Bond Elute chromatography eluting with ethyl acetate/hexane 1:3 to give the title compound (0.032g, 11% yield) as a yellow oil ($M^+ = 318$).

^1H nmr δ 1.3 (6H, d), 2.7 (3H, s), 5.4 (1H, m), 6.4 (1H, d), 7.0 (4H, m), 8.3 (1H, s) ppm.

EXAMPLE 4

This Example illustrates the preparation of 5-methyl-6-(4-fluoro-phenylthio)-7-chloro-s-1,2,4-triazolo[1,5-a]pyrimidine (Compound No. 3, Table 1)

Stage 1

A mixture of 5-methyl-6-bromo-s-triazolo[1,5-a]pyrimidin-7-ol (0.700g), 4-fluorothiophenol (0.390g) and anhydrous potassium carbonate (0.415g) in ethylene glycol (5ml) was stirred under a nitrogen atmosphere at 140-150°C for 5 hours. The reaction mixture was
25 cooled to room temperature, acidified to pH1 and the solid filtered off to give 5-methyl-6-(4-fluoro-phenylthio)-s-1,2,4-triazolo[1,5-a]pyrimidin-7-ol as a white solid which was used in the next stage without further purification.

Stage 2

The crude 5-methyl-6-(4-fluoro-phenylthio)-s-1,2,4-triazolo[1,5-a]pyrimidin-7-ol
30 (0.39g) from Stage 1 and phosphoryl chloride (5ml) were refluxed for 23 hours and allowed to cool down to room temperature. The resulting red solution was poured carefully onto

crushed ice, extracted with chloroform, washed with water and dried over anhydrous magnesium sulphate. Removal of the solvent gave a red residue that was purified by column chromatography (silica gel eluted with ethyl acetate/hexane 1:1) and HPLC (eluting with ethyl acetate/hexane 2:5) to give the title compound (0.036g) as a white solid ($M^+ = 295$).

5 ^1H nmr δ 2.8 (3H, s), 7.0 (2H, t), 7.2 (2H, m), 8.5 (1H, s) ppm.

EXAMPLE 5

This Example illustrates the preparation of (Compound No. 22, Table 1)

Stage 1

A solution of bromine (4.1ml) in glacial acetic acid (6ml) was added dropwise to a solution
10 of 7-hydroxy-s[1,2,4]triazolo[1,5-a]pyrimidin-5(1*H*)-one, (18.0g) in glacial acetic acid (600ml) with stirring at room temperature. After complete addition, the solution was stirred at room temperature for 3 hours. The solid was separated by filtration, washed with ethanol and air dried to give 5-methyl-6-bromo-s-triazolo[1,5-a]pyrimidin-7-ol (19.2g, 71% yield) as a pale white solid: M^+ 236; M.P. >256°C.

15 Stage 2

A mixture of 6-bromo-7-hydroxy-s- [1,2,4]triazolo[1,5-a]pyrimidin-5(1*H*)-one (10g), piperidine (7ml), potassium carbonate (5 g) in DMF (80ml) was stirred overnight at 100°C. The yellow thick suspension was cooled to ambient temperature and evaporated to dryness under reduced pressure. The residue was resuspended in ethanol at 60°C for about an hour.
20 After filtration the mother liquor was evaporated to dryness to yield 6-*N*-piperidino-7-hydroxy-s[1,2,4]triazolo[1,5-a]pyrimidin-5(1*H*)-one (4.9 g , 80%) as pale yellow solid: M^+ 299; M.P. 255°C; ^1H nmr (D_2O) δ 7.78 (1H, s) ppm.

Stage 3

Phosphoryl chloride (35ml) was added dropwise, with caution, to 6-*N*-piperidino-7-hydroxy-s- [1,2,4]triazolo[1,5-a]pyrimidin-5(1*H*)-one (3.5g). After complete addition the
25 mixture was refluxed for 2 hours, cooled to room temperature and poured carefully with stirring onto crushed ice. The resulting red solution was extracted with diethyl ether, washed with water, dried and the solvent removed to give 5,7-dichloro-6-*N*-piperidino-s-triazolo[1,5-a]pyrimidine (3.60g, 70% yield) as an yellow oil.

30 M^+ 272; ^1H nmr (CDCl_3) δ 1.48-1.75 (6H, m), 3.02-3.14 (4H, m), 8.48 (1H, s) ppm.

Stage 4

(S)-2,2,2-Trifluoro-1-methyl-ethylamine (830 mg) was added dropwise to a solution of 5,7-dichloro-6-piperidino-s-triazolo[1,5-a]pyrimidine (500 mg) in dry DMF (30 ml) at 70°C. The reaction was stirred for 12 hours, poured into ice-cold water and extracted with ether. The ether extracts were washed with water, dried over anhydrous magnesium sulphate and the ether removed to give the title compound (448 mg, 70% yield) as a pale yellow solid: M^+ 349; M.P. 127°C.

EXAMPLE 6

This Example illustrates the preparation of (Compound No. 28, Table 1)

Stage 1

10 A mixture of 6-bromo-7-hydroxy-s [1,2,4]triazolo[1,5-a]pyrimidin-5(1*H*)-one (5 g), 4-fluoro-phenol (2 g), potassium carbonate (2.5 g) in DMF (50ml) was stirred overnight at 100°C. The yellow thick suspension was cooled to ambient temperature and evaporated to dryness under reduced pressure. The residue was resuspended in ethanol at 60°C for about an hour. After filtration the mother liquor was evaporated to dryness to yield 6-(4-fluorophenoxy)-7-hydroxy-s- [1,2,4]triazolo[1,5-a]pyrimidin-5(1*H*)-one (2.25 g, 48%) as pale yellow solid:

M^{-1} 261, M^{+1} 263; M.P. >256°C; ^1H nmr (D_2O) δ 7.18-7.24 (4H, m), 7.85 (1H, s) ppm.

Stage 2

20 Phosphoryl chloride (20 ml) was added dropwise, with caution, to 6-(4-fluorophenoxy)-7-hydroxy-s- [1,2,4]triazolo[1,5-a]pyrimidin-5(1*H*)-one (2 g). After complete addition the mixture was refluxed for 3 hours, cooled to room temperature and poured carefully with stirring onto crushed ice. The resulting red solution was extracted with diethyl ether, washed with water, dried and the solvent removed to give 5,7-dichloro-6-(4-fluorophenoxy)-s-triazolo[1,5-a]pyrimidine (1.32 g, 57% yield) as a yellow solid:

25 M.P. 130°C; ^1H nmr (CDCl_3) δ 6.74-6.78 (2H, m), 6.94-7.04 (2H, m), 8.52 (1H, s) ppm.

Stage 3

(S)-2,2,2-Trifluoro-1-methyl-ethylamine (385 mg) was added dropwise to a solution of 5,7-dichloro-6-(4-fluorophenoxy)-s-triazolo[1,5-a]pyrimidine (255 mg) in dry DMF (30ml) at ambient temperature. The reaction was stirred for 12 hours, poured into ice-cold water and extracted with ether. The ether extracts were washed with water, dried over anhydrous magnesium sulphate and the ether removed to give the title compound (286 mg, 89% yield) as a pale brown solid: M^{-1} 374; M.P. 156°C

EXAMPLE 7

This Example illustrates the fungicidal properties of compounds of formula (I). The compounds were tested against a variety of foliar fungal diseases of plants. The technique employed was as follows.

5 Plants were either grown in John Innes Potting Compost (No.1 or 2) in 4cm diameter, 3.5cm depth minipots or on an artificial, cellulose based growing medium. The test compounds were individually formulated as a solution either in acetone or acetone/ethanol (1:1 by volume) which was diluted in reverse osmosis water to a concentration of 75 or 100ppm (that is, 0.75 or 1mg of compound in a final volume of 10ml) immediately before
10 use. When foliar sprays were applied to monocotyledonous crops, TWEEN 20 (0.05% by volume) was added. TWEEN is a registered trade mark.

Individual compounds of formula (I) were applied as a foliar (Folr) application (where the chemical solution was applied to the foliage of the test plants by spraying the plant to maximum droplet retention); as a systemic (Syst) application (where the chemical
15 solution, 10ml, was applied as a root drench treatment) or as a stem (Stem) application (where the chemical solution was applied to the stems of the test plants by spraying the plants to run off).

These tests were carried out against *Plasmopara viticola* (PLASVI) and *Uncinula necator* (UNCINE), on vines; *Phytophthora infestans lycopersici* (PHYTIN) and *Botrytis cinerea* (BOTRCI), on tomatoes; *Venturia inaequalis* (VENTIN), on apples; *Blumeria graminis f.sp. tritici* (ERYSGT), *Stagonospora nodorum* (LEPTNO) and *Puccinia triticina* (PUCCRT), on wheat; and *Pyricularia oryzae* (PYRIOR) and *Rhizoctonia solani* (RHIZSO), on rice. Each treatment was applied to two or more replicate plants for *Plasmopara viticola*, *Phytophthora infestans lycopersici*, *Botrytis cinerea*, *Uncinula necator* and *Venturia*
25 *inaequalis* and in all tests where the cellulose growing medium was employed. In mini pot tests on *Blumeria graminis f.sp. tritici*, *Stagonospora nodorum*, *Puccinia triticina*, *Rhizoctonia solani* and *Pyricularia oryzae* two replicate pots each containing 6 to 10 plants were used for each treatment. The plants were inoculated with a calibrated fungal spore suspension one or two days before (Erad) or 6 hours, one day or two days after (Prot)
30 chemical application.

After chemical application and inoculation, the plants were incubated under high humidity conditions and then put into an appropriate environment to allow infection to

proceed, until the disease was ready for assessment. The *Blumeria graminis f.sp. tritici* plants were inoculated using a 'shake' inoculation technique. The *Uncinula necator* plants were inoculated using a 'blowing' inoculation technique. For *Plasmopara viticola*, the plants were reincubated under high humidity conditions for 24 hours prior to assessment. The time period
5 between chemical application and assessment varied from five to fourteen days according to the disease and environment. However, each individual disease was assessed after the same time period for all compounds.

Assessments were performed on a single leaf of each of the two replicate plants for *Plasmopara viticola* and *Venturia inaequalis* and on each of two leaves on each of the
10 replicate plants for *Phytophthora infestans lycopersici* and *Botrytis cinerea*. Assessments were performed on a single leaf of each of the three replicate plants for *Uncinula necator*. For *Blumeria graminis f.sp. tritici*, *Stagonospora nodorum*, *Puccinia trititica* and *Pyricularia oryzae* assessments were carried out collectively on the plants in each replicate pot or cellulose medium. For *Rhizoctonia solani*, the number of infected plants in each of two
15 replicate pots was assessed.

The disease level present (that is, the percentage leaf area covered by actively sporulating disease) or percentage of infected plants per pot was assessed visually. For each treatment, the assessed values for all its replicates were meaned to provide mean disease values. Untreated control plants were assessed in the same manner.

20 The following are examples of the compounds tested that showed plant fungicidal activity against one or more of the diseases: compounds 1, 2, 3, 6, 21-25, 27, 28, 30, 31, 33-35 of Table 1.

EXAMPLE 8

This Example illustrates the fungicidal properties of compounds of formula (I), where the
25 compounds were tested against a variety of foliar fungal diseases of plants in a leaf disk assay, with methods described below. Test compounds were dissolved in DMSO, and diluted into water to 200 ppm.

Erysiphe graminis f.sp. hordei (barley powdery mildew): barley leaf segments were placed on agar in a 24-well plate and sprayed with a solution of the test compound. After allowing to
30 dry completely, for between 12 and 24 hours, the leaf disks were inoculated with a spore suspension of the fungus. After appropriate incubation the activity of a compound was assessed four days after inoculation as preventive fungicidal activity.

Erysiphe graminis f.sp. tritici (wheat powdery mildew): wheat leaf segments were placed on agar in a 24-well plate and sprayed with a solution of the test compound. After allowing to dry completely, for between 12 and 24 hours, the leaf disks were inoculated with a spore suspension of the fungus. After appropriate incubation the activity of a compound was
5 assessed four days after inoculation as preventive fungicidal activity.

Pyricularia oryzae (rice blast): rice leaf segments were placed on agar in a 24-well plate and sprayed with a solution of the test compound. After allowing to dry completely, for between 12 and 24 hours, the leaf disks were inoculated with a spore suspension of the fungus. After appropriate incubation the activity of a compound was assessed four days after inoculation as
10 preventive fungicidal activity.

Botrytis cinerea (grey mould): bean leaf disks were placed on agar in a 24-well plate and sprayed with a solution of the test compound. After allowing to dry completely, for between 12 and 24 hours, the leaf disks were inoculated with a spore suspension of the fungus. After appropriate incubation the activity of a compound was assessed four days after inoculation as
15 preventive fungicidal activity.

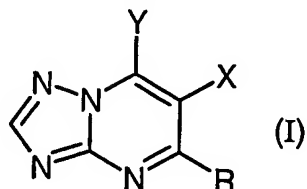
Phytophthora infestans (late blight of potato on tomato): tomato leaf disks were placed on water agar in a 24-well plate and sprayed with a solution of the test compound. After allowing to dry completely, for between 12 and 24 hours, the leaf disks were inoculated with a spore suspension of the fungus. After appropriate incubation the activity of a compound
20 was assessed four days after inoculation as preventive fungicidal activity.

Plasmopara viticola (downy mildew of grapevine): grapevine leaf disks were placed on agar in a 24-well plate and sprayed a solution of the test compound. After allowing to dry completely, for between 12 and 24 hours, the leaf disks were inoculated with a spore suspension of the fungus. After appropriate incubation the activity of a compound was
25 assessed seven days after inoculation as preventive fungicidal activity.

The following compounds from Table 1 gave greater than 60% control of disease: *Erysiphe graminis f.sp. hordei*, compounds 22, 25, 31, 34; *Erysiphe graminis f.sp. tritici*, compounds 22, 25, 34, 37, 49; *Pyricularia oryzae*, compounds 22, 25, 28, 29, 34, 38, 49, 57, 59; *Botrytis cinerea*, compounds 26, 49, 52, 59; *Plasmopara viticola*, compounds 29, 35, 38, 49, 54, 55,
30 56, 57; *Phytophthora infestans*, compounds 28; *Pythium ultimum*, compounds 52.

CLAIMS

1. The use as a plant fungicide of a compound of the general formula (I):

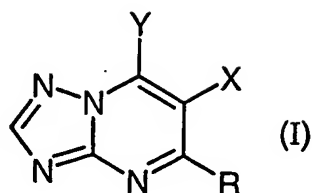


- wherein R is H, halo, C₁₋₈ alkyl or cyano; X and Y are independently halo, C₁₋₈ alkoxy, C₁₋₈ alkylthio, aryloxy, arylthio, heteroaryloxy, heteroarylthio, aryl(C₁₋₄)alkoxy, heteroaryl(C₁₋₄)alkoxy, aryl(C₁₋₄)alkylthio, heteroaryl(C₁₋₄)alkylthio, C₁₋₈ alkylamino, C₂₋₈ alkenylamino, C₂₋₈ alkynylamino, di(C₁₋₈)alkylamino, di(C₂₋₈)alkenylamino, di(C₂₋₈)alkynylamino, C₂₋₈ alkenyl(C₂₋₈)alkynylamino C₂₋₈ alkynyl(C₁₋₈)alkylamino or C₂₋₈ alkenyl(C₁₋₈)alkylamino arylamino, aryl(C₁₋₈ alkyl)amino, heteroarylamino, heteroaryl(C₁₋₈ alkyl)amino, aryl(C₁₋₄)alkylamino, aryl(C₁₋₄)alkyl(C₁₋₈ alkyl)amino, heteroaryl(C₁₋₄)alkylamino, heteroaryl(C₁₋₄)alkyl (C₁₋₈ alkyl)amino, morpholino or piperidino, or Y is hydroxy, provided that when X is C₁₋₈ alkoxy, aryloxy, morpholino or piperidino, R and Y are not both halo; any of the foregoing alkyl, alkenyl, alkynyl, aryl, heteroaryl, morpholino or piperidino groups or moieties being optionally substituted.
2. The use as a plant fungicide of a compound of the general formula (I) according to claim 1 wherein R is H, halo, C₁₋₈ alkyl or cyano; X and Y are independently halo, C₁₋₈ alkoxy, C₁₋₈ alkylthio, aryloxy, arylthio, heteroaryloxy, heteroarylthio, aryl(C₁₋₄)alkoxy, heteroaryl(C₁₋₄)alkoxy, aryl(C₁₋₄)alkylthio, heteroaryl(C₁₋₄)alkylthio, C₁₋₈ alkylamino, C₂₋₈ alkenylamino, C₂₋₈ alkynylamino, di(C₁₋₈)alkylamino, arylamino, aryl(C₁₋₈ alkyl)amino, heteroarylamino, heteroaryl(C₁₋₈ alkyl)amino, aryl(C₁₋₄)alkylamino, aryl(C₁₋₄)alkyl(C₁₋₈ alkyl)amino, heteroaryl(C₁₋₄)alkylamino or heteroaryl(C₁₋₄)alkyl (C₁₋₈ alkyl)amino or Y is hydroxy, morpholino or piperidino, provided that when X is other than halo, R and Y are not both halo; any of the foregoing alkyl, alkenyl, alkynyl, aryl, heteroaryl, morpholino or piperidino groups or moieties being optionally substituted.

3. The use as a plant fungicide of a compound of the general formula (I) according to claim 1 wherein R is H, halo, C₁₋₈ alkyl or cyano; X is halo, C₁₋₈ alkylthio, arylthio, heteroaryloxy, heteroarylthio, aryl(C₁₋₄)alkylthio, heteroaryl(C₁₋₄)alkylthio, C₁₋₈ alkylamino, C₂₋₈ alkenylamino, C₂₋₈ alkynylamino, di(C₁₋₈)alkylamino, arylamino, aryl(C₁₋₈ alkyl)amino, heteroarylamino, heteroaryl(C₁₋₈ alkyl)amino, aryl(C₁₋₄)alkylamino, aryl(C₁₋₄)alkyl(C₁₋₈ alkyl)amino, heteroaryl(C₁₋₄)alkylamino or heteroaryl(C₁₋₄)alkyl (C₁₋₈ alkyl)amino; and Y is halo, hydroxy, C₁₋₈ alkoxy, C₁₋₈ alkylthio, aryloxy, arylthio, heteroaryloxy, heteroarylthio, aryl(C₁₋₄)alkoxy, heteroaryl(C₁₋₄)alkoxy, aryl(C₁₋₄)alkylthio, heteroaryl(C₁₋₄)alkylthio, C₁₋₈ alkylamino, C₂₋₈ alkenylamino, C₂₋₈ alkynylamino, di(C₁₋₈)alkylamino, arylamino, aryl(C₁₋₈ alkyl)amino, heteroarylamino, heteroaryl(C₁₋₈ alkyl)amino, aryl(C₁₋₄)alkylamino, aryl(C₁₋₄)alkyl(C₁₋₈ alkyl)amino, heteroaryl(C₁₋₄)alkylamino or heteroaryl(C₁₋₄)alkyl (C₁₋₈ alkyl)amino, morpholino or piperidino; any of the foregoing alkyl, alkenyl, alkynyl, aryl, heteroaryl, morpholino or piperidino groups or moieties being optionally substituted.
4. The use as a plant fungicide of a compound of the general formula (I) according to any one of the preceding claims wherein R is H, halo or C₁₋₄ alkyl.
5. The use as a plant fungicide of a compound of the general formula (I) according to any one of the preceding claims wherein when one of X or Y is aryloxy, arylthio, heteroaryloxy, heteroarylthio, aryl(C₁₋₄)alkoxy, heteroaryl(C₁₋₄)alkoxy, aryl(C₁₋₄)alkylthio, heteroaryl(C₁₋₄)alkylthio, arylamino, aryl(C₁₋₈ alkyl)amino, heteroarylamino, heteroaryl(C₁₋₈ alkyl)amino, aryl(C₁₋₄)alkylamino, aryl(C₁₋₄)alkyl(C₁₋₈ alkyl)amino, heteroaryl(C₁₋₄)alkylamino or heteroaryl(C₁₋₄)alkyl(C₁₋₈ alkyl)amino the other is halo, C₁₋₈ alkoxy, C₁₋₈ alkylthio, C₁₋₈ alkylamino, di(C₁₋₈)alkylamino, or, in the case of Y, hydroxy.
6. The use as a plant fungicide of a compound of the general formula (I) according to claim 1 wherein R is H, halo, C₁₋₈ alkyl or cyano; X is halo, C₁₋₈ alkoxy, C₁₋₈ alkylthio, C₁₋₈ alkylamino or di(C₁₋₈)alkylamino and Y is aryloxy, arylthio, heteroaryloxy, heteroarylthio, aryl(C₁₋₄)alkoxy, heteroaryl(C₁₋₄)alkoxy, aryl(C₁₋₄)alkylthio, heteroaryl(C₁₋₄)alkylthio, C₁₋₈ alkylamino, C₂₋₈ alkenylamino, C₂₋₈ alkynylamino,

- di(C₁₋₈)alkylamino, arylamino, aryl(C₁₋₈ alkyl)amino, heteroarylamino, heteroaryl(C₁₋₈ alkyl)amino, aryl(C₁₋₄)alkylamino, aryl(C₁₋₄)alkyl(C₁₋₈ alkyl)amino, heteroaryl(C₁₋₄)-alkylamino, heteroaryl(C₁₋₄)alkyl(C₁₋₈ alkyl)amino, morpholino or piperidino; any of the foregoing alkyl moieties being optionally substituted with halo and any of the foregoing aryl or heteroaryl groups being optionally substituted with halo, C₁₋₄ alkyl, C₁₋₄ alkoxy, halo(C₁₋₄)alkyl, halo(C₁₋₄)alkoxy, cyano, nitro, amino, C₁₋₄ alkylamino or di(C₁₋₄)alkylamino.
- 5
7. The use as a plant fungicide of a compound of the general formula (I) according to claim 1 wherein R is H, halo, C₁₋₈ alkyl or cyano X is aryloxy, arylthio, heteroaryloxy, heteroarylthio, aryl(C₁₋₄)alkoxy, heteroaryl(C₁₋₄)alkoxy, aryl(C₁₋₄)alkylthio, heteroaryl(C₁₋₄)alkylthio, C₁₋₈ alkylamino, C₂₋₈ alkenylamino, C₂₋₈ alkynylamino, di(C₁₋₈)alkylamino, arylamino, aryl(C₁₋₈ alkyl)amino, heteroarylamino, heteroaryl(C₁₋₈ alkyl)amino, aryl(C₁₋₄)alkylamino, aryl(C₁₋₄)alkyl(C₁₋₈ alkyl)amino, heteroaryl(C₁₋₄)-alkylamino, or heteroaryl(C₁₋₄)alkyl(C₁₋₈ alkyl)amino; and Y is halo, hydroxy, C₁₋₈ alkoxy, C₁₋₈ alkylthio, C₁₋₈ alkylamino or di(C₁₋₈)alkylamino; any of the foregoing alkyl moieties being optionally substituted with halo and any of the foregoing aryl or heteroaryl groups being optionally substituted with halo, C₁₋₄ alkyl, C₁₋₄ alkoxy, halo(C₁₋₄)alkyl, halo(C₁₋₄)alkoxy, cyano, nitro, amino, C₁₋₄ alkylamino or di(C₁₋₄)-alkylamino.
- 10
- 15
- 20
8. The use as a plant fungicide of a compound of the general formula (I) according to claim 1 wherein R is halo; X is phenoxy, phenylthio, heteroaryloxy, heteroarylthio, morpholino or piperidino; and Y is C₁₋₈ alkylamino, C₂₋₈ alkenylamino, C₂₋₈ alkynylamino, di(C₁₋₈)alkylamino, di(C₂₋₈)alkenylamino, di(C₂₋₈)alkynylamino, C₂₋₈ alkenyl(C₂₋₈)alkynylamino C₂₋₈ alkynyl(C₁₋₈)alkylamino or C₂₋₈ alkenyl(C₁₋₈)alkylamino; any of the foregoing alkyl, alkenyl, alkynyl, phenyl, heteroaryl, morpholino or piperidino groups or moieties being optionally substituted.
- 25
9. The use as a plant fungicide of a compound of the general formula (I) wherein R is halo; X is phenylthio, heteroaryloxy or heteroarylthio; and Y is halo; any of the foregoing phenyl or heteroaryl moieties being optionally substituted.
- 30

10. A compound of general formula (I):



- wherein R is H, halo, C₁₋₈ alkyl or cyano; X and Y are independently halo, C₁₋₈ alkoxy, C₁₋₈ alkylthio, aryloxy, arylthio, heteroaryloxy, heteroarylthio, aryl(C₁₋₄)alkoxy, heteroaryl(C₁₋₄)alkoxy, aryl(C₁₋₄)alkylthio, heteroaryl(C₁₋₄)alkylthio, C₁₋₈ alkylamino, C₂₋₈ alkenylamino, C₂₋₈ alkynylamino, di(C₁₋₈)alkylamino, arylamino, aryl(C₁₋₈ alkyl)amino, heteroarylamino, heteroaryl(C₁₋₈ alkyl)amino, aryl(C₁₋₄)alkylamino, aryl(C₁₋₄)alkyl(C₁₋₈ alkyl)amino, heteroaryl(C₁₋₄)alkylamino or heteroaryl(C₁₋₄)alkyl(C₁₋₈ alkyl)amino or Y is hydroxy, morpholino or piperidino; any of the foregoing alkyl, alkenyl, alkynyl, aryl, heteroaryl, morpholino or piperidino groups or moieties being optionally substituted; provided that when X is other than halo, R and Y are not both halo, that when X is bromo and R is methyl, Y is not diethylamino or 3-(diethylamino)-propylamino, that when X is chloro and R is methyl, Y is not benzylamino and that when X is bromo or chloro and R is H or methyl, Y is not chloro or hydroxy.
11. A compound of general formula (I) wherein R is H, halo, C₁₋₈ alkyl or cyano; X is halo, C₁₋₈ alkylthio, arylthio, heteroaryloxy, heteroarylthio, aryl(C₁₋₄)alkylthio, heteroaryl(C₁₋₄)alkylthio, C₁₋₈ alkylamino, C₂₋₈ alkenylamino, C₂₋₈ alkynylamino, di(C₁₋₈)alkylamino, arylamino, aryl(C₁₋₈ alkyl)amino, heteroarylamino, heteroaryl(C₁₋₈ alkyl)amino, aryl(C₁₋₄)alkylamino, aryl(C₁₋₄)alkyl(C₁₋₈ alkyl)amino, heteroaryl(C₁₋₄)alkylamino or heteroaryl(C₁₋₄)alkyl(C₁₋₈ alkyl)amino; and Y is halo, hydroxy, C₁₋₈ alkoxy, C₁₋₈ alkylthio, aryloxy, arylthio, heteroaryloxy, heteroarylthio, aryl(C₁₋₄)alkoxy, heteroaryl(C₁₋₄)alkoxy, aryl(C₁₋₄)alkylthio, heteroaryl(C₁₋₄)alkylthio, C₁₋₈ alkylamino, C₂₋₈ alkenylamino, C₂₋₈ alkynylamino, di(C₁₋₈)alkylamino, arylamino, aryl(C₁₋₈ alkyl)amino, heteroarylamino, heteroaryl(C₁₋₈ alkyl)amino, aryl(C₁₋₄)alkylamino, aryl(C₁₋₄)alkyl(C₁₋₈ alkyl)amino, heteroaryl(C₁₋₄)alkylamino or heteroaryl(C₁₋₄)alkyl(C₁₋₈ alkyl)amino, morpholino or piperidino; any of the foregoing alkyl,

alkenyl, alkynyl, aryl, heteroaryl, morpholino or piperidino groups or moieties being optionally substituted; provided that when X is bromo and R is methyl, Y is not diethylamino or 3-(diethylamino)-propylamino, that when X is chloro and R is methyl, Y is not benzylamino and that when X is bromo or chloro and R is H or methyl, Y is not chloro or hydroxy.

12. A compound of the general formula (I) as defined in claim 1 wherein R is halo; X is phenoxy, phenylthio, heteroaryloxy, heteroarylthio, morpholino or piperidino; and Y is C₁₋₈ alkylamino, C₂₋₈ alkenylamino, C₂₋₈ alkynylamino, di(C₁₋₈)alkylamino, di(C₂₋₈)-alkenylamino, di(C₂₋₈)alkynylamino, C₂₋₈ alkenyl(C₂₋₈)alkynylamino C₂₋₈ alkynyl-(C₁₋₈) alkylamino or C₂₋₈ alkenyl(C₁₋₈)alkylamino; any of the foregoing alkyl, alkenyl, alkynyl, phenyl, heteroaryl, morpholino or piperidino groups or moieties being optionally substituted.
13. A compound of the general formula (I) as defined in claim 1 wherein R is halo; X is phenylthio, heteroaryloxy or heteroarylthio; and Y is halo; any of the foregoing phenyl or heteroaryl moieties being optionally substituted.
14. A plant fungicidal composition comprising a fungicidally effective amount of a compound as defined in claim 1 and a suitable carrier or diluent therefor.
15. A method of combating or controlling phytopathogenic fungi which comprises applying to a plant, to a seed of a plant, to the locus of the plant or seed or to soil or to any other plant growth medium, a fungicidally effective amount of a compound as defined in claim 1 or a composition as defined in claim 14.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 02/04734

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 A01N43/90

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 A01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

CHEM ABS Data, WPI Data, EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,X	WO 02 50077 A (HENRICH MARIELOUISE ; MAULER-MACHNIK ASTRID (DE); HILGERS PETRA (DE) 27 June 2002 (2002-06-27) the whole document ---	1-15
X	YASUO MAKISUMI: "SYNTHESIS OF POTENTIAL ANTICANCER AGENTS VI. REACTIVITY OF 6-BROMO-S-TRIAZOLO 2,3-APYRIMIDINES" CHEMICAL AND PHARMACEUTICAL BULLETIN, TOKYO, JP, vol. 9, 1961, pages 814-817, XP001040489 ISSN: 0009-2363 the whole document ---	10,11,14
P,X	WO 01 96314 A (BASF AG) 20 December 2001 (2001-12-20) the whole document ---	1-15
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☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

* Special categories of cited documents :

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- *E* earlier document but published on or after the international filing date
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- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
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Date of the actual completion of the international search

6 December 2002

Date of mailing of the international search report

16/12/2002

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax (+31-70) 340-3016

Authorized officer

Bertrand, F

INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 02/04734

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,X	WO 01 96341 A (BASF AG) 20 December 2001 (2001-12-20) the whole document ---	1-15
X	US 6 255 309 B1 (PFRENGLE WALDEMAR ET AL) 3 July 2001 (2001-07-03) the whole document ---	1-15
X	US 6 242 451 B1 (PEES KLAUS-JUERGEN) 5 June 2001 (2001-06-05) cited in the application the whole document ---	1-15
X	US 5 985 883 A (PEES KLAUS-JUERGEN) 16 November 1999 (1999-11-16) cited in the application the whole document ---	1-15
X	WO 99 48893 A (AMERICAN CYANAMID CO) 30 September 1999 (1999-09-30) cited in the application the whole document ---	1-15
X	EP 0 945 453 A (AMERICAN CYANAMID CO) 29 September 1999 (1999-09-29) cited in the application the whole document ---	1-15
X	WO 99 41255 A (AMERICAN CYANAMID CO) 19 August 1999 (1999-08-19) cited in the application the whole document ---	1-15
X	US 6 020 338 A (PFRENGLE WALDEMAR ET AL) 1 February 2000 (2000-02-01) the whole document ---	1-15
X	WO 98 46608 A (AMERICAN CYANAMID CO) 22 October 1998 (1998-10-22) cited in the application the whole document ---	1-15
X	WO 98 46607 A (AMERICAN CYANAMID CO) 22 October 1998 (1998-10-22) cited in the application the whole document ---	1-15
X	EP 0 834 513 A (AMERICAN CYANAMID CO) 8 April 1998 (1998-04-08) cited in the application the whole document ---	1-15

	-/--	

INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 02/04734

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 94 20501 A (SHELL INT RESEARCH ; PEES KLAUS JUERGEN (DE); BECHER HEINZ MANFRED) 15 September 1994 (1994-09-15) cited in the application the whole document ----	1-15
X	EP 0 613 900 A (SHELL INT RESEARCH) 7 September 1994 (1994-09-07) the whole document ----	1-15
X	EP 0 550 113 A (SHELL INT RESEARCH) 7 July 1993 (1993-07-07) cited in the application the whole document ----	1-15
X	EP 0 071 792 A (BASF AG) 16 February 1983 (1983-02-16) cited in the application the whole document ----	1-15
X	GB 1 148 629 A (HYDRIERWERK RODLEBEN VEB) 16 April 1969 (1969-04-16) cited in the application examples 4,5,14 -----	10,11,14

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/GB 02/04734

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
WO 0250077	A	27-06-2002	DE 10063115 A1 AU 3167602 A WO 0250077 A2	27-06-2002 01-07-2002 27-06-2002
WO 0196314	A	20-12-2001	AU 7056401 A WO 0196314 A1	24-12-2001 20-12-2001
WO 0196341	A	20-12-2001	AU 7844501 A WO 0196341 A2	24-12-2001 20-12-2001
US 6255309	B1	03-07-2001	NONE	
US 6242451	B1	05-06-2001	US 5985883 A FR 2784381 A1 JP 2000103790 A	16-11-1999 14-04-2000 11-04-2000
US 5985883	A	16-11-1999	FR 2784381 A1 JP 2000103790 A US 6242451 B1	14-04-2000 11-04-2000 05-06-2001
WO 9948893	A	30-09-1999	US 5981534 A AU 752669 B2 AU 3098599 A AU 735730 B2 AU 6867198 A BG 103805 A BR 9808531 A BR 9909009 A CA 2324154 A1 CN 1302299 T CZ 20003472 A3 EE 9900486 A EP 0975635 A1 EP 0945453 A1 EP 1066291 A1 HU 0001993 A2 HU 0101751 A2 JP 11322750 A JP 2001520650 T NO 994973 A NZ 500143 A PL 343176 A1 SK 141499 A3 WO 9948893 A1 US 6284762 B1	09-11-1999 26-09-2002 18-10-1999 12-07-2001 11-11-1998 30-06-2000 23-05-2000 28-11-2000 30-09-1999 04-07-2001 16-01-2002 15-06-2000 02-02-2000 29-09-1999 10-01-2001 28-10-2000 28-10-2001 24-11-1999 30-10-2001 13-10-1999 29-06-2001 30-07-2001 11-09-2001 30-09-1999 04-09-2001
EP 0945453	A	29-09-1999	AU 752669 B2 AU 3098599 A AU 735730 B2 AU 6867198 A BG 103805 A BR 9808531 A BR 9909009 A CA 2324154 A1 CN 1302299 T CZ 20003472 A3 EE 9900486 A EP 0975635 A1	26-09-2002 18-10-1999 12-07-2001 11-11-1998 30-06-2000 23-05-2000 28-11-2000 30-09-1999 04-07-2001 16-01-2002 15-06-2000 02-02-2000

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/GB 02/04734

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0945453	A	EP 0945453 A1	29-09-1999
		EP 1066291 A1	10-01-2001
		HU 0001993 A2	28-10-2000
		HU 0101751 A2	28-10-2001
		JP 11322750 A	24-11-1999
		JP 2001520650 T	30-10-2001
		NO 994973 A	13-10-1999
		NZ 500143 A	29-06-2001
		PL 343176 A1	30-07-2001
		SK 141499 A3	11-09-2001
		WO 9948893 A1	30-09-1999
		US 6284762 B1	04-09-2001
WO 9941255	A 19-08-1999	US 6020338 A	01-02-2000
		AU 750489 B2	18-07-2002
		AU 2595299 A	30-08-1999
		BR 9907863 A	24-10-2000
		CA 2320304 A1	19-08-1999
		CN 1292790 T	25-04-2001
		CZ 20002933 A3	17-04-2002
		EP 1054888 A1	29-11-2000
		HU 0100885 A2	28-06-2001
		JP 2002503664 T	05-02-2002
		PL 342576 A1	18-06-2001
		WO 9941255 A1	19-08-1999
US 6020338	A 01-02-2000	AU 750489 B2	18-07-2002
		AU 2595299 A	30-08-1999
		BR 9907863 A	24-10-2000
		CA 2320304 A1	19-08-1999
		CN 1292790 T	25-04-2001
		CZ 20002933 A3	17-04-2002
		EP 1054888 A1	29-11-2000
		HU 0100885 A2	28-06-2001
		JP 2002503664 T	05-02-2002
		PL 342576 A1	18-06-2001
		WO 9941255 A1	19-08-1999
WO 9846608	A 22-10-1998	AU 735730 B2	12-07-2001
		AU 6867198 A	11-11-1998
		BG 103805 A	30-06-2000
		BR 9808531 A	23-05-2000
		CN 1257502 T	21-06-2000
		EE 9900486 A	15-06-2000
		EP 0975635 A1	02-02-2000
		HU 0001993 A2	28-10-2000
		JP 2001520650 T	30-10-2001
		NO 994973 A	13-10-1999
		NZ 500143 A	29-06-2001
		PL 336164 A1	05-06-2000
		SK 141499 A3	11-09-2001
		TR 9902552 T2	22-05-2000
		TW 460476 B	21-10-2001
		WO 9846608 A1	22-10-1998
		ZA 9803054 A	11-10-1999
WO 9846607	A 22-10-1998	AT 202779 T	15-07-2001
		AU 6576898 A	11-11-1998

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/GB 02/04734

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9846607 A		DE 69801048 D1	09-08-2001
		DE 69801048 T2	14-03-2002
		DK 975634 T3	24-09-2001
		EP 0975634 A1	02-02-2000
		ES 2160408 T3	01-11-2001
		GR 3036714 T3	31-12-2001
		PT 975634 T	28-12-2001
		WO 9846607 A1	22-10-1998
		ZA 9803055 A	11-10-1999
EP 0834513 A	08-04-1998	US 5817663 A	06-10-1998
		AT 221069 T	15-08-2002
		DE 69714171 D1	29-08-2002
		EP 0834513 A2	08-04-1998
		JP 10152489 A	09-06-1998
		US 5965561 A	12-10-1999
WO 9420501 A	15-09-1994	AT 159722 T	15-11-1997
		AU 690899 B2	07-05-1998
		AU 6258094 A	26-09-1994
		BR 9405988 A	26-12-1995
		CA 2157293 A1	15-09-1994
		CN 1119015 A ,B	20-03-1996
		CZ 9502233 A3	17-01-1996
		DE 69406538 D1	04-12-1997
		DK 699200 T3	20-07-1998
		WO 9420501 A1	15-09-1994
		EP 0699200 A1	06-03-1996
		HK 1004332 A1	20-11-1998
		HU 73163 A2	28-06-1996
		IL 108747 A	12-03-1999
		JP 8507505 T	13-08-1996
		NZ 262729 A	26-01-1996
		PL 310467 A1	11-12-1995
		RU 2130459 C1	20-05-1999
		SG 48860 A1	18-05-1998
		SK 106895 A3	05-06-1996
		US 5854252 A	29-12-1998
		ZA 9401485 A	10-11-1994
EP 0613900 A	07-09-1994	EP 0613900 A1	07-09-1994
		AT 153025 T	15-05-1997
		AU 672267 B2	26-09-1996
		AU 5633294 A	08-09-1994
		BG 61647 B1	27-02-1998
		BG 98637 A	31-01-1995
		BR 9400808 A	01-11-1994
		CA 2116946 A1	05-09-1994
		CN 1094407 A	02-11-1994
		DE 69403119 D1	19-06-1997
		DE 69403119 T2	28-08-1997
		DK 613900 T3	23-06-1997
		ES 2101429 T3	01-07-1997
		GR 3023587 T3	29-08-1997
		HK 1001054 A1	22-05-1998
		HU 68050 A2	29-05-1995
		IL 108731 A	18-03-1997
		JP 7002861 A	06-01-1995

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/GB 02/04734

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0613900	A	NZ 250955 A	27-04-1995
		OA 9891 A	15-09-1994
		RO 112869 B1	30-01-1998
		RU 2126408 C1	20-02-1999
		SG 48897 A1	18-05-1998
		US 5756509 A	26-05-1998
		ZA 9401484 A	10-11-1994
EP 0550113	A	07-07-1993	07-07-1993
		EP 0550113 A2	07-07-1993
		EP 0782997 A2	09-07-1997
		GR 3033916 T3	30-11-2000
		AT 159256 T	15-11-1997
		AT 192154 T	15-05-2000
		AU 667204 B2	14-03-1996
		AU 3043592 A	01-07-1993
		BR 9205172 A	06-07-1993
		CA 2086404 A1	01-07-1993
		CN 1075144 A ,B	11-08-1993
		CN 1141119 A ,B	29-01-1997
		DE 69222746 D1	20-11-1997
		DE 69222746 T2	12-02-1998
		DE 69230977 D1	31-05-2000
		DE 69230977 T2	09-11-2000
		DK 550113 T3	09-02-1998
		DK 782997 T3	07-08-2000
		ES 2108727 T3	01-01-1998
		ES 2147411 T3	01-09-2000
		GR 3025920 T3	30-04-1998
		HK 1010105 A1	23-06-2000
		HU 217349 B	28-01-2000
		IL 104244 A	13-07-1997
		JP 5271234 A	19-10-1993
		NZ 245581 A	26-07-1995
		PL 297160 A1	06-09-1993
		PL 171579 B1	30-05-1997
		PT 782997 T	29-09-2000
		RU 2089552 C1	10-09-1997
		SG 47563 A1	17-04-1998
		US 5593996 A	14-01-1997
		ZA 9210043 A	28-07-1993
EP 0071792	A	16-02-1983	17-02-1983
		DE 3130633 A1	17-02-1983
		AT 11539 T	15-02-1985
		AU 553663 B2	24-07-1986
		AU 8665982 A	10-02-1983
		CA 1180329 A1	01-01-1985
		CS 226748 B2	16-04-1984
		DD 202093 A5	31-08-1983
		DE 3262143 D1	14-03-1985
		DK 341682 A ,B,	02-02-1983
		EP 0071792 A2	16-02-1983
		GR 76193 A1	03-08-1984
		HU 188325 B	28-04-1986
		IE 53269 B1	28-09-1988
		JP 1634879 C	20-01-1992
		JP 2061955 B	21-12-1990
		JP 58043974 A	14-03-1983
		US 4567263 A	28-01-1986

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/GB 02/04734

Patent document cited in search report		Publication date	Patent family member(s)		Publication date
EP 0071792	A		ZA	8205498 A	27-07-1983
GB 1148629	A	16-04-1969	DE	1620694 A1	03-12-1970
			DE	1792811 C2	30-12-1982